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**APPLICATION OF LIQUID-LIQUID EXTRACTION
TO SOME ORGANIC PROCESSES**

**BY
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TO SOME ORGANIC PROCESSES

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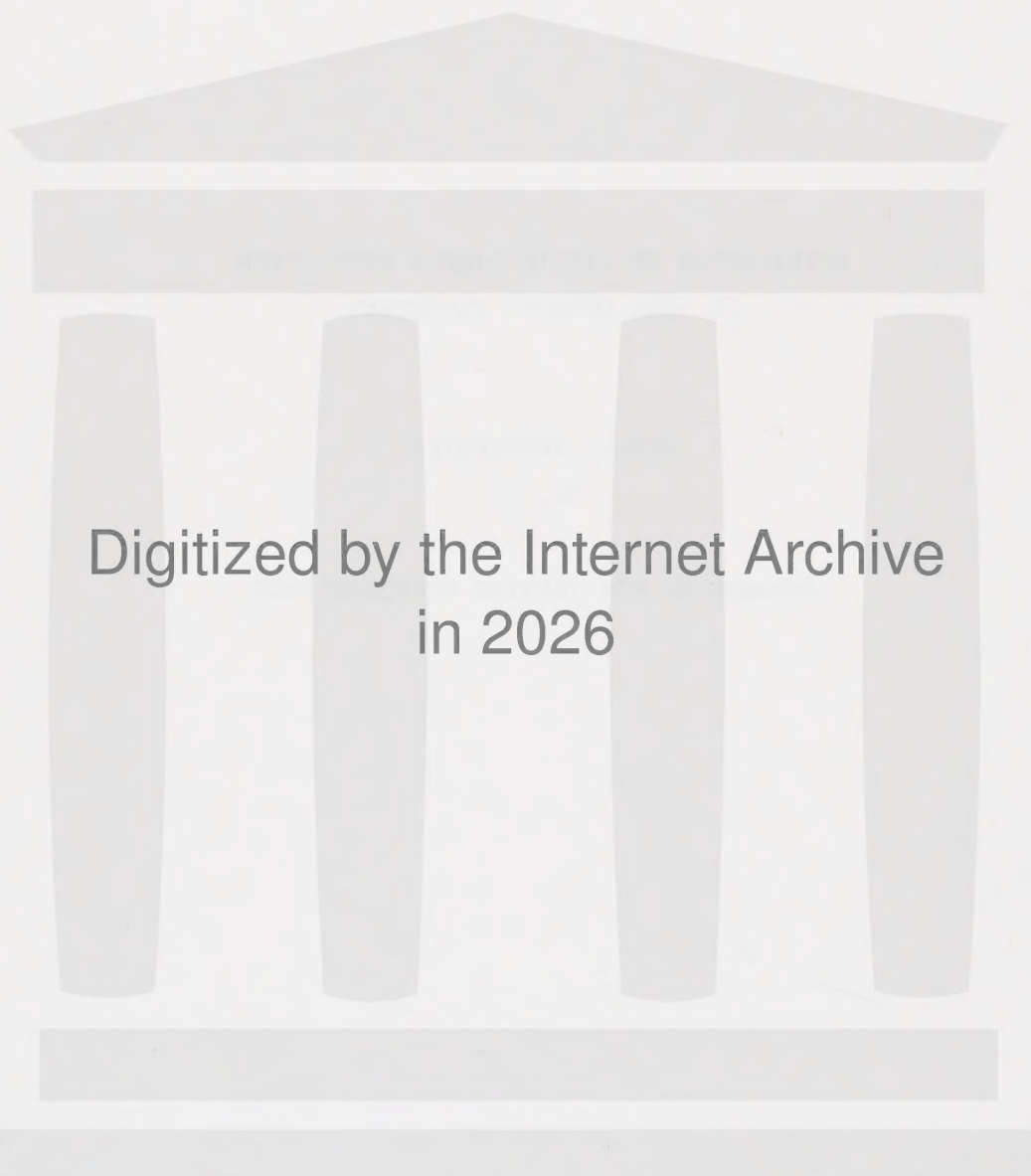
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Abstract

Liquid extraction have been applied to some organic processes. In the production of p-nitrobenzoic acid a process is proposed in which an effluent consisting of nitric acid and organic pollutants is treated in such a way that nitric acid can be recovered.

The conventional recovery of citric acid from fermentation broth is highly complex. An alternative process using liquid extraction is shown to be technically feasible.

An extraction-distillation process have thoroughly been investigated concerning energy requirement for the treatment of condensate effluents containing organic substances.

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APPLICATION OF LIQUID-LIQUID EXTRACTION TO SOME ORGANIC PROCESSES

Ronald Wennersten, Department of Chemical Engineering, Lund Institute of Technology, Lund, Sweden.

The thesis consists of this summary and of the following papers:

I. Wennersten, R.

Extraction of organic pollutants from an effluent stream in the manufacture of p-nitrobenzoic acid.

International Solvent Extraction Conference, Liège, 1980.

II. Wennersten, R.

A new method for the purification of citric acid by liquid-liquid extraction.

International Solvent Extraction Conference, Liège, 1980.

III. Wennersten, R.

The extraction of citric acid from fermentation broth using a solution of a tertiary amine.

Report LUTKDH/(TKKA-3002)/1-11/(1981), Dept of Chem Eng, Lund Institute of Technology, 1981.

IV. Wennersten, R., Zacchi, G. and Aly, G.

A solvent extraction-distillation process for treatment of condensate effluents containing organic substances and economic recovery of by-products.

2nd World Congress of Chemical Engineering, Montréal, 1981.

INTRODUCTION

Liquid extraction is a unit operation in which the constituents of a liquid solution can be separated by contact with another liquid. As a recovery method for wastewater treatment and a separation route in organic processes, liquid extraction is not as widely used as distillation, which has always dominated because of its role in the petroleum and petrochemicals industries. Nevertheless, the last two decades have seen an increasing interest in liquid extraction in a wide range of industries. The dramatic rise in energy costs has in some cases changed the economic balance in favour of extraction for some separations which can be achieved either by extraction or distillation. Thermal damage to the product, separation factors too close to unity and the need for extreme conditions of temperature and/or pressure when distillation is to be used are other factors that often disfavour distillation.

At first glance, liquid extraction may not look as attractive as a carbon bed or a resin bed adsorption process for the removal of organics from dilute water-solutions. This is especially true if simple laboratory experiments are taken as models.

Activated carbon or resin beads can be added to the solution and most of the organic substances removed in one step. If however, some arbitrary solvent is added in one step, the result may not look too convincing. First the organic substances are only partially removed. Second the substances that are removed end up contaminating the solvent. And third the water is left saturated with the solvent that was used. An analogous unfair comparison can be made for distillation. The substances which could have been removed directly with steam stripping, are replaced by a solvent which has to be removed by steam stripping. There are many examples where discouraging comparisons have excluded solvent extraction at an early stage when a separation technique has been chosen.

The present work on the extraction of organic substances, will hopefully make a small contribution of assistance to chemical engineers who wish to undertake a serious investigation of the feasibility of a solvent extraction process.

DESIGN CRITERIA

1. General

Although the liquid extraction process might look simple from an engineering point of view and has relatively low equipment costs the design of an economically attractive process requires a complex strategy taking account of many dependent variables. There are numerous examples in which an improper comparison between liquid extraction and other separation techniques has been made because of a quite unsystematic investigation of the solvent selection step. The substance to be extracted, the solute, and the extracting solvent, made up of extractant and a diluent, interact in such a complicated way that the extraction step cannot be isolated from the recovery steps when the solvent is to be selected. There are at least three integrated stages which must be taken into consideration:

- liquid-liquid contact
- solvent recovery
- raffinate cleanup

In the extraction of organic components, these three steps can all, as will be shown, turn up to be equally important for operating- and capital costs. Design calculations cannot be made, on the basis of distribution coefficients only. Thus several cases have shown that the "optimum" economic approach was neither obvious nor anticipated in preliminary studies.

The initial requirement in the development of a solvent extraction process for the recovery or separation of organic substances is a knowledge of the feed composition and flow rate and of the restrictions on the product quality and raffinate composition. With these starting conditions fixed a preliminary solvent selection can be made from solvents representing different process configurations such as:

- low-boiling solvents
- high-boiling solvents
- solvents from which the solute is stripped back into an aqueous phase

There is of course no "universal solvent" and solvent selection must be done individually for each separation problem. The specific choice must be based on a general knowledge of the different interactions in both phases.

Among the desirable features for an extraction solvent are the following:

1. It should have a high capacity for the species being separated into it.
2. It should be selective, dissolving one of the key components being separated to a large extent while not dissolving the other key components to any large extent.
3. It should have a low mutual solubility with water.
4. It should be easily regenerated.
5. It should have suitable physical properties such as density, viscosity and surface tension.
6. It should be relatively inexpensive, non-toxic, and non-corrosive.

Obviously no solvent will be best from all these viewpoints, and the selection of a desirable solvent involves a compromise between these and other factors. When a preliminary selection has been made a secondary screening can be performed based on simplified calculations on minimum energy requirement since the capital costs for similar process configurations will not vary too much.

In the final selection rigorous calculations must be carried out together with laboratory tests on phase separation properties, chemical stability, the verification of equilibrium data used in the calculations etc. At this stage the data obtained have to be examined critically to ensure that there is sufficient potential for the project to be carried to the next phase. If sufficient information has been collected for a conceptual flowsheet to be drawn, a decision can then be made on whether to run a pilot plant. From pilot plant data the process can be scaled-up according to principles given in the literature. This outline of the principles of designing a solvent extraction process is general but some of the individual steps require experience and effective aids such as computer programs and experimental equipment. Some of the difficult steps will be discussed in greater detail below.

2. Defining the separation problem

The industrial stream to be treated, the feed will not be an analytical grade solute dissolved in water, but will often contain several known and unknown substances, both organic and inorganic. To be able to make a first

selection of possible solvents it is necessary to make a classification of the individual substances present in the feed and of the groups of substances with chemical similarities, for instance, paraffins, aromatics, salts, etc.

Thus, in a process developed in our department (1), now in operation for the production of a certain quality of tri-methylol propane (TMP), the feed contained salts, TMP and higher organic substances. The following questions had to be answered:

What is the pH of the solution? Which acids or bases are present?

Are there additives such as surfactants which will affect the phase separation properties?

Are there solids present? What is their nature?

Are there restrictions concerning product quality or raffinate compositions?

Are there any toxic components?

What is the stability of the substances?

When the criteria above have been stated one can faithfully proceed to the next step.

3. Primary solvent selection

At this stage it is advisable to make a literature search, preferably on a computer-based system or in a literature source book (2) to answer the question: What is the state of art concerning the extraction of the substance of interest or of similar materials?

A preliminary selection of solvents must be based on an estimate of chemical interactions which could be of importance. These are mainly solute-solvent and solvent-solvent interactions. Solute-solvent interactions are markedly dependent on the natures of the solute and the solvent. The interaction is least when both are non-polar, it becomes stronger as the polarity of the molecules increases, and it is strongest when there are interactions due to the formation of hydrogen bonds, charge transfer complexes, or coordination complexes. It is desirable to find a solvent which can form strong, specific interactions with the solute to be extracted. The well-known rule-of-thumb that like dissolves like does not

always apply. The solubilities of non-polar substances are sometimes larger in polar solvents than in non-polar solvents. The explanation could be that although the solvent-solvent interactions may be large in a polar solvent, the gain in energy due to the non-polar solute-polar solvent interaction can be still larger. In such a case this larger gain outweighs the disadvantage of the elimination of the solvent-solvent interaction and a higher solubility can be expected. The classification of the solvents according to their chemical structure and functional groups has been described elsewhere (3) and will not be treated here. If specific chemical interactions are present, as in the case where an acid is extracted with a basic solvent, the complex formed may exhibit a low solubility in the solvent. In this case the solvent should comprise both an extractant (in this case the base) and a diluent which has a high solubility for the complex. This synergistic effect of a diluent can also be a result of breaking of the solvent-solvent interactions. As well as having a synergistic effect on the extraction, the diluent can also affect the physical properties of the solvent in a positive way. The "optimal" diluent will have the following characteristics:

- It improves the distribution of the solute to be extracted.
- It improves the selectivity.
- It increases the density difference between the phases and lowers the viscosity of the solvent.

At this stage it may not be possible to distinguish any promising process configuration for the recovery of the solvent. From the general criteria given above a selection should be made of a number of solvents representing the following classes

- Solvents having a lower boiling point than the solute (low-boiling solvents).
- Solvents having a higher boiling point than the solute (high-boiling solvents).
- Solvents from which the solute could be stripped back into an aqueous phase perhaps utilising a temperature-shift or a chemical reaction.

The recovery process must also be kept in mind and fundamental vapour-liquid data such as the formation of azeotropes should be examined.

Azeotropic data can be found in the literature (4) but is sometimes contradictory. Finally solvents that are unstable, toxic, expensive and high-grade should be avoided unless the product price is high and the feed flow rate is low.

4. Secondary solvent selection

As mentioned above, quantitative optimization of all solvent properties is a very difficult and time-consuming procedure, since many process-design alternatives must be considered for each solvent. Consequently, the solvent screening strategy used in this work was to identify a group of solvents that appeared to have the most promise as extractants for the solute. Approximate calculations, using computer program PRIMCALC, were then performed to evaluate these solvents by estimating the minimum energy requirements. Rigorous computations, using the computer program DESTEX, were then made for a limited number of promising solvents, to quantify the effects of various process-design alternatives.

Computer program PRIMCALC

PRIMCALC is a group of computer programs specially designed in order to simplify calculation of energy requirements in combined extraction-distillation processes for the recovery of organic chemicals from diluted aqueous solutions. As an example on running the program for the water-furfural-solvent system (5), the following assumptions were made:

- A. *Solvent extraction*: Having specified the degree of solute recovery a phase ratio of 1.5 times $(V/L)_{\min}$ was used. A constant K_D -value was assumed, and chosen as the lowest value in the concentration range considered. The solute does not affect the mutual solubility between solvent and water.
- B. *Regeneration of lower-boiling solvents*: The solvent recovery column is assumed to produce pure components, i.e. pure solute as bottoms and pure solvent as distillate. A minimum reflux ratio is used in this column, and in the solvent stripping column to reach azeotropic concentration in the distillate. In this latter column, the lowest steam consumption which can be tolerated for practical reasons, is taken as 1 % of its feed.
- C. *Regeneration of higher-boiling solvents*: A simplified process scheme was used for the recovery of solute from the extract phase. Minimum steam consumption in the first column is calculated for the separation of the water-solvent azeotrope from solvent. A stream consisting of all

of the solvent and solute existing in the extract phase is passed through in a second column giving pure solute as distillate. Water and solute are separated in two columns using a minimum reflux ratio. Purification of the raffinate phase is dealt with as described for the case using lower-boiling solvents.

Computer program DESTEX

For simulation of the various process configurations investigated, a computer program for steady-state calculations of general distillation-extraction systems was used. This computer program, DESTEX, is based on the principles of modular composition. Flowsheets of arbitrary complexity may be assembled by connecting together the various unit operation equipment available in the unit cell. The unit cell comprises a plate, a make-up vessel, a reboiler, partial and total condensers, a mixing vessel for liquid, an extraction stage, and a liquid separation vessel. Information on phase equilibria can be supplied in two different ways. If the equations already available in the program used (Wilson and UNIQUAC) are to be used some binary parameters must be given. Alternatively, the user may supply his own subprogrammes specifying this information.

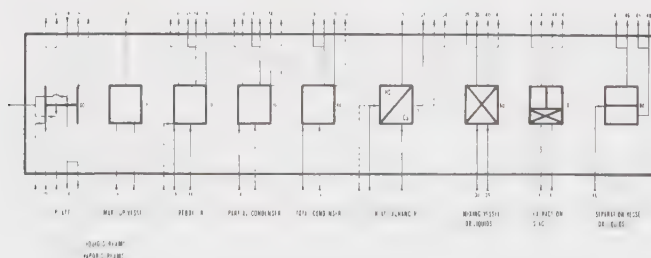


Fig. 1: DESTEX'S Unit cell

The reliability of the calculations is very much dependent on the available equilibrium data. In some cases these are obtainable from the literature but often they have to be estimated in some way or determined in the laboratory. If analysis of the solute is easy to carry out liquid-liquid equilibrium (LLE) data can be obtained quite easily with a mechanical shake bath. In a specially constructed apparatus this can also be done at

temperatures above the boiling points. Vapour-liquid equilibrium (VLE) measurements are time consuming and the UNIFAC method was found to be valuable here.

For LLE-data there are still many parameters missing in UNIFAC and great care must be taken when using the existing ones since their estimation is sometimes based on a very limited number of solvents.

The general relationship between solvent capacity and solvent selectivity for physically interacting solvent extraction systems can be inferred from the Scatchard-Hildebrand equation (6) for predicting activity coefficients from solubility parameters. The derivation of that equation assumes that the molecules have similar sizes, that they undergo interaction through dispersion forces alone, and that they are not associated in solution. For the liquid mixtures encountered in extraction processes these assumptions do not hold and the Scatchard-Hildebrand equation can be considered only a very rough first approximation with limited use for screening extraction solvents.

There have been a number of efforts to modify the solubility parameter concept so as to take into account the different types of intermolecular forces (dipole-dipole, dipole-induced dipole, and dispersion forces) as well as hydrogen bonding for the prediction of solubilities and activity coefficients. Wennersten et al. (7) have developed a computer program which calculates activity coefficients at infinite dilution for solutes in a number of industrial solvents. The Helsenstill-van Winkle correlation (8) was slightly modified using 2-3 dimensional solubility parameters. The program was tested for phenol in 19 different solvents. The results show that the modified correlation gives a better agreement with experimental values for most of the solvents than the original correlation. This modification can be regarded as a complement to the UNIFAC method where some gaps still exist.

5. Laboratory tests

Some important features of the solvents selected cannot be estimated but have to be evaluated in laboratory tests. One important question which may be decisive for the technical feasibility of a process is the phase separation properties. In some of the processes investigated these were poor and the extracting agent and the diluent had to be carefully selected on

the bases of laboratory runs in specially designed mixer-settler units. In these the mixer and the settler were separated enabling the feed and the solvent flows to be stopped so that the coalescence rate could be observed. From these runs a preferred phase continuity could also be determined. The mixer-settler units, which are made of glass, can be connected to each other so that a counter-current process can be adopted. In such runs the equilibrium data used in the calculations can be verified and problems connected with the formation of crud can be quantified. It is important that fresh feed is used since aging processes may occur. This is especially important when fermentation broth is to be used as feed. It was sometimes found to be beneficial to condition the solvent to improve the phase separation. This was done by contacting the fresh solvent with a solution similar to that which was to be used in the test work. For the recovery cycle, batch distillation units or a small scale continuous column with variable reflux was adopted. In these tests the chemical stability of the solvent and the other substances can also be investigated. From the laboratory tests a preliminary calculation can be made of the technical and economical feasibility of the process. If the full scale plant is small a scale-up can often be safely accomplished.

6. Pilot plant operations

If laboratory runs are successful one has to decide whether to carry out pilot plant operations or not. This decision is dependent on prior knowledge and experience with similar processes. As the objective of running the pilot plant is to establish sufficient data for a safe scale-up calculation, the feed flow rate is also important. If the plant is to be small, enough data may be collected from the laboratory runs. Equipment chosen for pilot plant operations should closely approximate the commercially available equipment that will eventually be used. It is important that the pilot plant is operated for a sufficient length of time to obtain meaningful data.

The selection of solvent extraction equipment has been treated earlier (9) and will not be discussed here.

SUMMARY OF THE PRESENT WORK

Liquid extraction have been applied to some organic processes. In the production of p-nitrobenzoic acid a process is proposed in which an effluent consisting of nitric acid and organic pollutants is treated in such a way that nitric acid can be recovered.

The conventional recovery of citric acid from fermentation broth is highly complex. An alternative process using liquid extraction is shown to be technically feasible.

An extraction-distillation process have thoroughly been investigated concerning energy requirement for the treatment of condensate effluents containing organic substances.

A summary of the processes investigated is given below.

PART I

p-Nitrobenzoic acid is produced by catalytic oxidation of p-nitrotoluene by dilute nitric acid in a tube reactor at high pressure and temperature. After crystallization of the acid the mother liquor containing 15 weight-% nitric acid and 1 weight-% organic impurities remains. The mother liquor from this particular process has been dumped in a nearby lake after neutralization. Biological treatment of the effluent is not possible since some of the pollutant material is biotoxic. The objective of this work was to study the possibility of adopting solvent extraction to reduce the impurities to such a level that the nitric acid could be recirculated to the reactor. The incentives for treating the mother liquor were thus both economic and environmental. The impurities consist of at least ten organic substances only a part of which was identified. As the nitric acid is to be recirculated to the reactor after treatment a design strategy was adopted in which the raffinate should be recirculated without raffinate stripping thus reducing both capital and operating costs. This puts some important restrictions on the choice of solvent. The solvent must have a very small solubility in the raffinate stream, not only for economic reasons, but also to avoid undesirable reactions in the reactor. Toluene is present in the feed to the reactor and shake tests revealed that toluene was an effective solvent for most of the impurities except for some di-nitrobenzoic acids. It was obvious that a more polar solvent must be used to extract these. o-Nitrotoluene is also present in the feed to the

reactor and this solvent is obtained as a nonsaleable byproduct within the company. Other solvents were also tested but o-nitrotoluene was the most promising. However its physical properties, a density close to that of the mother liquor and a rather high melting point, makes it unsuitable without a diluent. Mixtures of o-nitrotoluene and toluene gave the physical properties required and extracted the dinitrobenzoic acids to a sufficient extent, except for 2,6-dinitrobenzoic acid. To extract the latter it was found that a stronger Lewis base for instance tri-butyl-phosphate, is necessary. Recirculation tests showed that this substance can be allowed to build up to a higher concentration without any disturbances in the reactor. Mixer-settler runs in glass laboratory units showed that six stages and a phase ratio V/L of 0.56 was sufficient to extract more than 90 % of the impurities, which was the limit set. Using o-nitrotoluene as a component of the solvent also solved the problem of solvent recovery. Toluene now could be recovered by distillation since the impurities and o-nitrotoluene are higher boiling. Vacuum distillation was recommended for the recovery of toluene while the bottom product is incinerated. This example shows that the solvent selection is not a straight-forward and general process, but something which must be done individually for each case in order to determine the most economic process. With some minor modifications the process as developed here is that now in operation.

PART II AND III

Citric acid produced by fermentation is today recovered by a separation to remove the microorganisms and then several precipitation and washing stages. Technically this recovery process is highly complex, chemicals are consumed and calcium sulphate is obtained as an unsaleable byproduct. In the present work, described in parts II and III, the objective has been to study whether solvent extraction can be used as an alternative to precipitation for the recovery of citric acid.

Carbon-bonded oxygen-donor solvents like alcohols, ketones and esters are rather poor extractants for citric acid and their selectivity was found to be low. As the solvents have to be recovered by distillation, since they are low-boiling, the energy requirement in the recovery cycle will be high and considerable impurities will remain in the acid. Stronger Lewis bases, such as phosphoryl solvents and tertiary amines, were found to be both more effective and more selective. Extracting agents of this type are high-boiling and the citric acid has therefore to be recovered in a strip-

ping stage in which pure water re-extracts the acid from the solvent. The distribution coefficient is highly temperature dependent, hence the stripping is preferably accomplished at an elevated temperature.

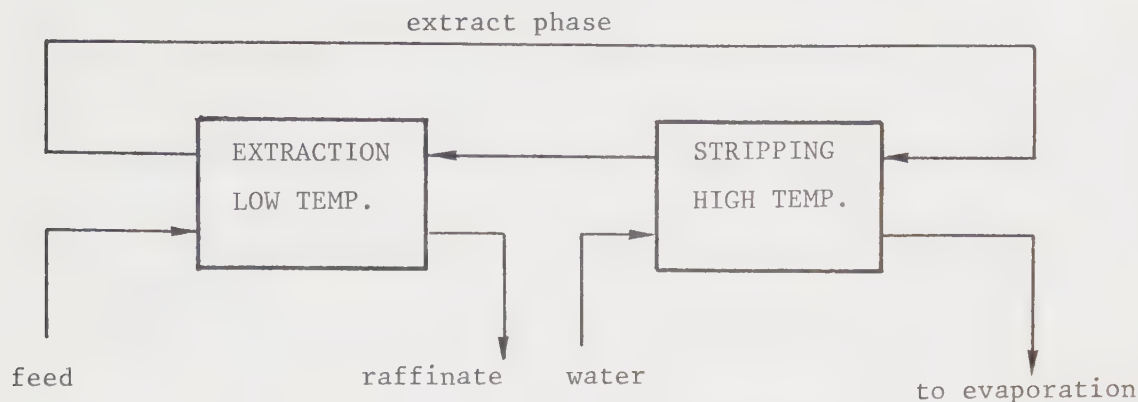


Fig. 2: Process for the recovery of citric acid

The amines give higher distribution coefficients at room temperature than the phosphoryl extractants. An important parameter here is the diluent, which has to be chosen with great care. Through a careful selection of diluent and phase ratio the extraction can be carried out in agitated columns. The stripping, which requires a temperature over 100°C, was done in a new type of equipment consisting of a plate heat exchanger and a separation vessel. As solvent we have suggested a tertiary amine of the type Alamine 336 dissolved in a nonpolar diluent.

PART IV

Several solvent extraction-distillation processes for treatment of sulphite pulping condensates and for economic recovery of byproducts, essentially furfural, methanol and acetic acid, have been investigated here. The investigation was carried out in the following three steps:

- solvent screening based on approximate calculations of energy requirement
- rigorous computer simulations
- experimental investigation in laboratory and pilot equipment

Calculations of separation processes, for recovery of organic solutes from dilute aqueous solutions, where solvent extraction and distillation are interconnected are extremely tedious without suitable computer programs. Two computer programs, PRIMCALC and DESTEX, were developed during the course of this work. These programs greatly facilitate the design calculation of combined solvent extraction-distillation processes.

Several separation routes were studied:

- neutralisation of the liquor and recovery of methanol and furfural by extraction
- fractionation of methanol and furfural followed by acetic acid extraction
- simultaneous extraction of furfural and acetic acid

Details of the design strategy that was adopted has been described elsewhere (10). The most energy saving solvents turned out to be:

- chloroform for the extraction of furfural (Fig. 3)
- high molecular tertiary amines dissolved in high-boiling alcohols for the extraction of acetic acid and
- ethyl acetate for the simultaneous extraction

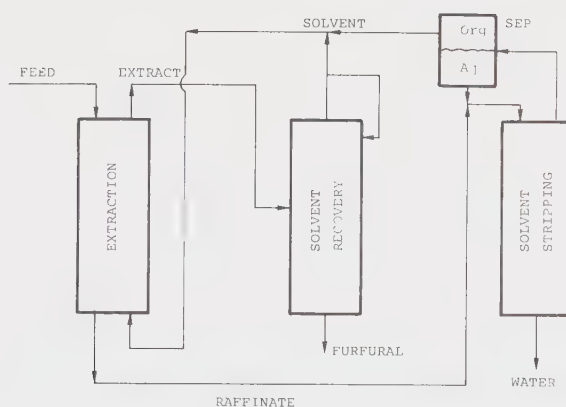


Fig. 3: Extraction of furfural with low-boiling solvents

The calculations clearly indicated that both LLE and VLE data play an equally important role in computing energy requirements for the overall process. This point is often overlooked and many papers base their solvent selection upon LLE data only.

As far as energy requirement in a separation process is concerned, combined solvent extraction-distillation process have a considerably greater potential than distillation alone. For each aqueous system, there will be a break-even concentration of the organic impurities below which this combination is more economic and above which distillation only should be applied.

A general recovery process for all sulphite condensates is not possible. Some specific parameters must be fixed, such as concentration levels and mutual concentrations of different solutes.

Laboratory runs must therefore be carried out with the specific condensate of interest.

FUTURE WORK

As a recovery method for waste-water treatment and a separation route in organic processes, liquid extraction is not as widely used as distillation. One of the reasons that has held back a wider application of liquid extraction is its inherent complexity. The extraction step is only a small part of a typical extraction process. A large part of the capital investment and nearly all of the energy requirement are in the solvent recovery steps. Moreover, extraction processes usually require pilot-plant development with solvent selection as a critical step.

Another drawback is the large hold-up of solvent in some applications. Solvents are often expensive and discrete stage contactors, involving phase separation at each stage, are usually in use.

Liquid membranes and the use of supercritical gases as extractants are new approaches to overcome some of these drawbacks. The liquid membrane technique is a simultaneous extraction/stripping process by means of a selective liquid membrane separating two miscible liquid phases. It can be achieved in the same contactor using only a minimal amount of solvent. The center of interest of possible applications appears to be in non-ferrous hydrometallurgy, biomedical engineering and waste-water treatment. There are some disadvantages to be offset against the advantages of liquid membranes: slow mass transfer and the need for breaking the multi-emulsion.

Compressed gases near or above their critical point may be used as solvents for organic substances. From a chemical engineering point of view they are of interest because their solvating power can be varied considerably by changing their density.

There are a number of suggestions given in the literature which relate to the use of compressed gases as solvents in extraction. Examples are decaffeination of raw coffee, extraction of nicotine from tobacco, separation of glycerides and recovery of ethanol from fermentation solutions.

Future work in prospect here will concern the recovery of organic acids and of ethanol produced from cellulosic materials. This will provide an opportunity for exploration of these new separation techniques.

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EXTRACTION OF ORGANIC POLLUTANTS FROM AN EFFLUENT
STREAM IN THE MANUFACTURE OF P-NITROBENZOIC ACID

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EXTRACTION OF ORGANIC POLLUTANTS FROM AN EFFLUENT STREAM IN THE MANUFACTURE OF P-NITROBENZOIC ACID

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ABSTRACT

Solvent extraction can successfully be applied to purify the mother liquor obtained in the production of p-nitrobenzoic acid. The mother liquor, which discharged earlier in a lake, is a dilute nitric acid solution containing some organic pollutants at low concentrations. A recovery process has been designed in which a mixture of toluene and o-nitrotoluene extracts the organic pollutants while the purified nitric acid is recycled to the main process. Toluene is recovered by vacuum distillation and o-nitrotoluene is burnt together with the organic pollutants.

INTRODUCTION

p-Nitrobenzoic acid, an intermediate product in the pharmaceutical industry, is manufactured in Sweden in one of the largest units in the world. It is produced by catalytic oxidation of p-nitrotoluene by dilute nitric acid in a tube reactor at high pressure and temperature. The p-nitrobenzoic acid is crystallized out of the reaction solution and the solid product is separated off in centrifuges, dried and packed. The mother liquor from the centrifuges contains 15 weight-% nitric acid and a total of about 1 weight-% organic pollutants that are more or less toxic, p-dinitrobenzene being the most dangerous.

The polluted mother liquor has been dumped in a nearby lake after neutralization. In the disposal of this stream there are both environmental and economic factors to be considered. The industry concerned recently received a notification from the Swedish environmental authorities that this effluent must be treated before discharge. Several methods for lowering

the organic content and recovery of nitric acid have been investigated. Adsorption by active carbon was thoroughly examined but the costs estimated were too high. Biological treatment of the effluent is not possible because of the toxicity of some of the pollutants. The mother liquor has also been recirculated within the process without treatment (with occasional bleed-off), but the build-up of p-nitrobenzene caused severe health problems among the people working in the factory.

This project (1) has studied the possibility of using solvent extraction to treat this effluent stream. The main objective has been to reduce the pollutants to such a level that the nitric acid can be recirculated to the reactor.

SOLVENT SELECTION

The mother liquor from the centrifuges has a temperature of 80°C and contains a large number of organic substances. Table 1 gives the identifiable pollutants. These are present at concentrations far below 1 weight-%. Some of these substances are quite polar and are able to form hydrogen bonds with water molecules.

Dinitrobenzoic acids	(2,6-, 2,4-, 3,5- and 3,4-DNBA)
Nitrobenzoic acids	(o-, m- and p-NBA)
Dinitrobenzenes	(m- and p-DNB)
Trinitrobenzene	(TNP)
Picric acid	
Nitrotoluenes	(o- and p-NT)
Dinitrotoluenes	(2,4- and 3,4-DNT)
Nitroxylenes	
Unidentified substances	

TABLE 1
Organic pollutants in mother liquor

There are some important restrictions on the choice of a solvent in this special case. The solvent must have a very limited solubility in the raffinate phase not only for economic reasons but also to avoid undesirable reactions in the reactor. For the same reason the solvent should be chemically related to the organic pollutants. Shake tests in an earlier stage of the investigation indicated that toluene, which is widely used within the company, could be a suitable solvent.

The tests showed that most of the pollutants could be extracted except for some of the benzoic acids. In order to extract these, it was necessary to find a more polar solvent. Within the company, o-nitrotoluene (o-NT) is obtained as a nonsaleable byproduct. However, o-NT has a density that is very close to that of the mother liquor. The melting point is also quite high (-2.9°C) which makes it unsuitable for storage outdoors.

Component	Conc. in raffinate phase, weight-%	Conc. in extract phase, weight-%	$K_D = \frac{C_{\text{extr}}}{C_{\text{raff}}}$
2,6-DNBA	0.0280	0.0002	0.01
	0.0270	0.0004	0.01
	0.0270	0.0005	0.02
	0.0250	0.0006	0.02
	0.0280	0.0008	0.03
2,4-DNBA	0.0530	0.0520	0.98
	0.1740	0.1320	0.76
	0.1690	0.2510	1.49
	0.2180	0.4030	1.85
	0.3760	0.4120	0.91
3,5-DNBA	0.0009	0.0013	1.44
	0.0060	0.0045	0.75
	0.0100	0.0064	0.64
	0.0050	0.0160	3.20
	0.0050	0.0340	6.80
3,4-DNBA	0.0020	0.0080	4.00
	0.0140	0.0400	2.86
	0.0250	0.0590	2.36
	0.0340	0.1170	3.44
	0.0480	0.1580	3.29
p-DNB	0.0003	0.0100	33.33
	0.0003	0.0210	70.00
	0.0005	0.0440	88.00
	0.0008	0.0750	93.75

TABLE 2

Distribution coefficients for organic pollutants in the mother liquor
(Solvent: 70 vol-% toluene + 30 vol-% o-NT, Temp.: 20°C)

Mixtures of o-NT with toluene offer a possibility of obtaining a solvent with the proper physical properties. Shake tests showed that a mixture of 70 vol-% toluene with 30 vol-% o-NT gave the physical properties required. The distribution coefficients, obtained with this mixture, are shown in table 2. As can be seen the hazardous substance p-DNB is readily extracted. The acids are able to form hydrogen bonds with water and, as expected have the lowest distribution coefficients; 2,6-DNBA has significantly lower K_D than the other acids. In order to study the relative importance of different attractive forces, 2,6-DNBA was extracted separately from a water solution (0.0123 weight-%) into 6 different solvents. The results of shake tests, carried out at 19.5°C and with a phase ratio of 1.0, are given in table 3.

The acids contain the strongly electron-attracting nitro group which gives them acceptor properties. Toluene on the other hand, acts as a π -donor, which means that the π -molecular orbitals can be shared. If more electron donating methyl groups are attached to the ring as in o-xylene and mesitylene, this donor character is enhanced. As can be seen in table 3 there is no difference in extraction capability between toluene, o-xylene and mesitylene. The conclusion would be that energies from π -complexes could be neglected in this case. A possible reason for this could be the steric interference between the two nitro groups and the carboxyl group. A close ring to ring attachment between 2,6-DNBA and the solvent molecules is then more difficult to establish. This steric interference will also affect the resonance in 2,6-DNBA in such a way that the electron attracting power of the nitro group is diminished. This effect can explain why 2,6-DNBA is extracted less than the other acids when o-NT is used as a solvent. Resonance effects should make 2,6-DNBA a weaker dipole than the other acids and this will make the dipole-dipole interaction to o-NT smaller.

Extraction of 2,6-DNBA to a higher degree requires a stronger Lewis base, like tri-n-butyl phosphate (TBP) where the phosphoryl oxygen can form hydrogen bonds with the carboxyl group. Consequently, as can be seen in table 3, TBP extracts 2,6-DNBA better than methyl-iso-butyl ketone since the carbonyl group is a weaker Lewis base than the phosphoryl group.

Solvents, vol-%	Conc. in raffinate phase, weight-%
70% Toluene + 30% o-NT	0.0121
70% Toluene + 30% Methyl-iso-butyl ketone	0.0118
70% Toluene + 30% Tri-n-butyl phosphate	0.0070
Toluene	0.0121
o-xylene	0.0121
Mesitylene	0.0122

TABLE 3
Extraction of 2,6-DNBA by different solvents

MIXER-SETTLER RUNS

Mixer-settler runs were carried out in laboratory glass units. In order to avoid further crystallisation the feed was kept at a temperature of 80°C which is that of the mother liquor leaving the centrifuges. No heat was added to the mixer-settler stages and the temperature in the stages therefore varied from 40°C in the first stage to about 25°C in the last stage. The solvent, which was kept at 20°C, consisted of 70 vol-% toluene and 30 vol-% o-NT. The density of the solvent was 957 kg/m³ (20°C) and that of the feed 1080 kg/m³ (65°C). In 6 mixer-settler stages, countercurrent extraction was investigated with 3 different phase ratios as shown in table 4 below.

Flow of raffinate phase, L, g/min	Flow of extract phase, V, g/min	V/L
29	28	0.97
26	44	1.69
50	28	0.56

TABLE 4
Conditions for mixer-settler runs

A complete run analysis using a phase ratio of 0.56 is shown in table 5. As expected, most of the 2,6-DNBA stays in the raffinate phase. This component can however, be allowed to be built up to a higher concentration level without any disturbances in the reactor as can be seen. Some of the

recirculated components may also be destroyed in the reactor if the concentration is raised, so that a constant level can be obtained without any bleed-off.

SOLVENT REGENERATION

Solvent regeneration includes the separation of toluene from the o-NT and the organic pollutants which are burnt. Toluene is recycled to extraction after being mixed with 30 vol-% o-NT. Three different methods for distillation have been investigated; namely continuous and batch steam distillation and vacuum distillation. The advantage of using vacuum distillation is that, by keeping a low temperature, the risk of thermal decomposition of the organic compounds is minimized. The advantage of using steam distillation is that a low temperature can be used at normal pressure but

Component	Raffinate phase conc., weight-%	Extract phase conc., weight-%	Feed conc., weight-%
2,6-DNBA	0.025	0.003	0.030
2,4-DNBA	0.105	0.620	0.680
o-NBA	0.010	0.025	0.030
Picric acid	-	0.170	0.100
3,5-DNBA	-	0.005	0.010
m-NBA	0.005	0.350	0.260
p-NBA	0.005	0.180	0.120
3,4-DNBA	-	0.230	0.170
o-NT	0.050	-	0.0002
p-NT	0.001	-	0.004
Nitroxylenes	0.001	0.008	0.004
p-DNB	0.001	0.0505	0.0235
m-DNB + unid.*	0.0008	0.0760	0.0230
2,4-DNT	-	0.100	0.055
3,4-DNT	-	0.008	0.004
TNB	-	0.0140	0.006
Unidentified	0.0008	0.0245	0.0101

TABLE 5

Results from a mixer-settler run
(Number of stages: 6, V/L: 0.56)

*probably 2,6-DNT

this gives a higher steam consumption than vacuum distillation. Equilibrium data was calculated with a computer program AZTROP (2) which utilizes the UNIFAC model. Optimization and calculation of the required number of ideal distillation stages was carried out with another computer program DESTLA (3). From the calculations, vacuum distillation and continuous steam distillation turned out to be the best alternatives to carry out the separation, vacuum distillation having higher capital cost but lower operating cost. Considering the reliability of the calculations vacuum distillation must be recommended.

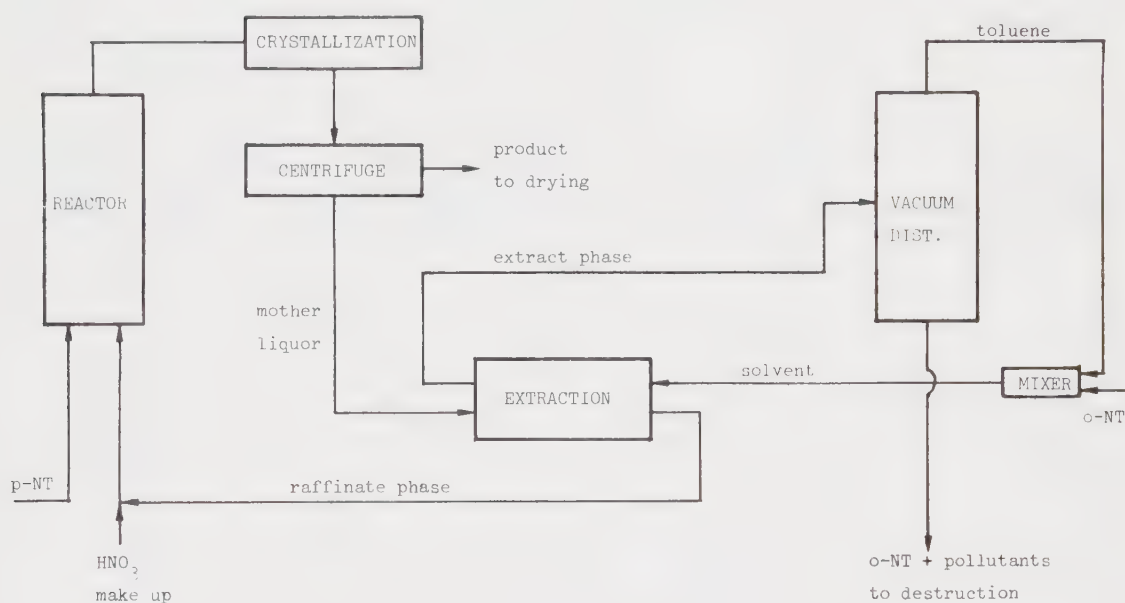


FIG. 1

Flow sheet for HNO_3 recovery from mother liquor

PROCESS DESIGN

Figure 1 shows the process flow sheet for purification of the mother liquor. From the centrifuges the mother liquor is fed to an extraction battery where the organic pollutants are extracted in counter-current mixer-settlers. The raffinate phase, mainly dilute nitric acid, is recycled to the reactor after make-up with nitric acid. The extract phase containing toluene, o-NT and organic pollutants is fed to a vacuum distillation tower. At the top, toluene is recovered and after adding fresh o-NT, is reused as solvent in the extraction. The bottom product consisting of o-NT and organic pollutants is sent to thermal destruction.

ANALYSIS

Analysis were carried out on a Waters Associates 440 HPLC using the column Bondapak C 18 (Reverse phase) and a flow of 1 ml/min.

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A NEW METHOD FOR THE PURIFICATION OF
CITRIC ACID BY LIQUID EXTRACTION

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A NEW METHOD FOR THE PURIFICATION OF CITRIC ACID BY LIQUID-LIQUID EXTRACTION

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ABSTRACT

Citric acid is commonly made by fermentation. The recovery of the acid from the aqueous fermentation solution is a complex process which gives calcium sulphate as a nonsaleable residue.

In this work the possibility of using solvent extraction for the recovery of citric acid from water solutions has been studied.

INTRODUCTION

Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid), $C_6H_8O_7$ is the most widely used organic acid in the food and pharmaceutical industries. It is also used to sequester ions, neutralise bases and as a buffer. Esters of citric acid are used commercially as plasticisers in the preparation of polymer compositions, protective coatings and adhesives.

Citric acid is produced by many yeasts, moulds and bacteria. With the development of fermentation technology, most citric acid is now produced by this technique. The acid is recovered from the aqueous fermentation solution by first separating the microorganisms and then precipitating the citrate ion as the insoluble calcium salt. Citric acid is then obtained by adding sulphuric acid. Technically the recovery of the product is a highly complex process. The calcium sulphate is an unsaleable residue. The main objective of this work (1) has been to study whether solvent extraction can be used as an alternative to precipitation for the recovery of citric acid from aqueous fermentation solutions.

SOLVENT SELECTION

The choice of a solvent affects the design of the whole process in a significant way, both in the extraction section and in the solvent recovery cycle. A solvent for industrial purposes where the product value is rather low must have a low price and high availability. For use in the food industry, the requirement of low toxicity is also important. Citric acid, having one hydroxy- and three carboxyl groups, is very soluble in water. To be able to extract citric acid from a water solution, the interaction energies between the solvent molecules and citric acid must be in the range of the hydrogen bonds which exist between water molecules and citric acid. There are three main classes of solvents which could be of interest in this special case; carbon-bonded oxygen-donor solvents, high molecular weight amines and phosphorus-bonded oxygen-donor solvents.

CARBON-BONDED OXYGEN-DONOR SOLVENTS

When extracting with these solvents the oxygen acts as a Lewis base which can solvate an organic acid. Solvents of this type are ethers, alcohols, ketones, aldehydes, and esters. Extraction of citric acid with solvents of this class has been frequently described in the literature (2-5). As can be seen from table 1, the distribution coefficients for citric acid (with 0.16 wt% feed conc.) are rather low.

Solvent	Distribution coefficient
n-Butanol	0.29
Ethyl acetate	0.1
Ethyl ether	0.1
Methyl-iso-butyl ketone	0.1
Methylethyl ketone	0.33
Cyclohexanone	0.21

TABLE 1
Distribution coefficients for citric acid (3)

With such low distribution coefficients a large number of contacting stages and a high V/L ratio are needed to extract the main part of the citric acid. Moreover, these solvents are relatively soluble in water and often they form azeotropes with water. The solvent recovery cycle will therefore be costly and this yields poor process economy.

HIGH MOLECULAR WEIGHT, ALIPHATIC AMINES

Smith and Page (6) have reported on acid-binding properties of long-chain aliphatic amines. The acid binding properties of these bases depend on the fact that their salts with acids are almost insoluble in water, but readily soluble in many organic solvents. They suggested also that these amines could be used for the recovery of valuable organic acids from biological materials as fermentation liquors. In our case however, shake tests using fermentation solutions showed that these solvents gave very stable emulsions which did not separate at all. Because of this no further tests were made with these solvents at this stage.

PHOSPHORUS-BONDED OXYGEN-DONOR SOLVENTS

These reagents contain the phosphoryl group which is a stronger Lewis base than the carbon-bonded oxygen group. Furthermore solvents belonging to this class co-extract less water and are less soluble in water than the first class. The basicity of the phosphoryl oxygen increases in the order: Trialkyl phosphate $((RO)_3P=O)$, dialkylalkyl phosphonate $((RO)_2RP=O)$, alkylalkyl phosphinate $((RO)R_2P=O)$, trialkyl phosphine oxide $(R_3P=O)$. Wardell and King (7) found that for the extraction of acetic acid from a 0.5 wt-% water solution, the basicity increased with the number of butoxy groups $(-OCH_2CH_2CH_2CH_3)$ according to table 2.

Compound	Number of butoxy groups	K_D
Tributyl phosphate	3	2.3
Dibutylbutyl phosphonate	2	2.7
Butyldibutyl phosphinate	1	-
Tributyl phosphine oxide	0	4.4*

TABLE 2

Effect of number of butoxy groups on the distribution of acetic acid.
*37.3 wt-% in Chevron Solvent 25. No diluent used for other solvents.

Tributyl phosphate is readily mixed with non-polar diluents such as kerosene, but to obtain higher concentrations of the phosphine oxides more polar solvents are needed. The separation of relatively volatile organic acids from these solvents can be easily achieved by means of distillation. This method can not however be applied to citric acid because of its high boiling point and tendency to decompose. Stripping using a base dissolved

in water would require a recovery process for the acid which is similar to that now used and nothing would be won. The possibility of using these solvents however, lies in the fact that the distribution coefficient is very dependent of temperature. This means that extraction can be carried out at one temperature and stripping at another temperature. The important parameter then turns out to be not so much K_D but the temperature dependence of K_D . As can be seen from table 3, this temperature dependence of K_D for trioctyl phosphine oxide (TOPO) is about the same as for tri-n-butyl phosphate (TBP).

To obtain higher solubilities of TOPO, a more polar solvent must be added which would result in higher solvent losses. TOPO is also very expensive compared with TBP. Among the phosphoryl reagents TBP has become the most widely used in industry. The availability and price make TBP the most promising solvent for this special application.

EXPERIMENTAL WORK

The high viscosity of TBP and the fact that its density is close to unity makes it necessary to use some kind of diluent with low viscosity and density. The choice of diluent affects the distribution coefficient, as can be seen in table 3. The highest values of K_D were obtained using ethers and ketones. As mentioned earlier the important parameter is the variation of K_D with temperature and this variation is more pronounced using hydrocarbons as diluents. The TBP concentration should be as high as possible, taking the phase separation properties into consideration. Two types of kerosenes have been used; namely Shellsol A and Shellsol H having aromatic contents of 99% and 16% respectively. K_D is somewhat higher using Shellsol H, probably because the interaction between the diluent and TBP is less. Figure 1 shows equilibrium curves for the system citric acid-water- 75 vol-% TBP in Shellsol A at 4 different temperatures.

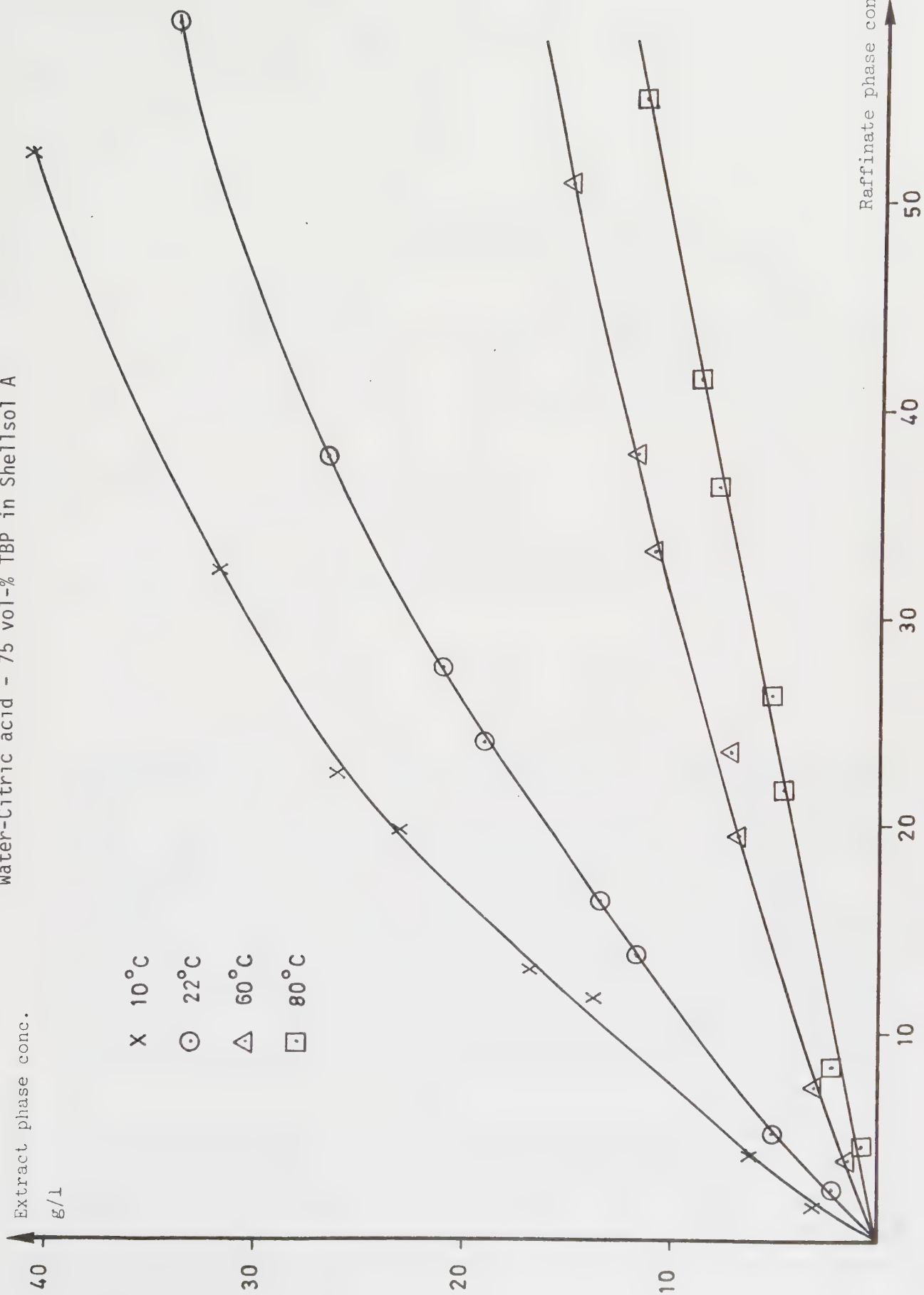
Solvent	Conc. of citric acid in water solution, M	Temperature °C	K_D
0.4 M TOPO in 50 vol-% n-heptane + 50 vol-% n-octanol	0.21	20.6	0.01
50 vol-% n-heptane + 50 vol-% n-octanol	0.21	20.6	0.001
0.2 M TOPO in Shellsol H	0.072 0.072	21.0 40.0	0.28 0.12
50 vol-% TBP + 50 vol-% di-iso-propylether	0.026 0.026 0.26 0.26	17.5 60.0 17.5 60.0	0.68 0.27 0.56 0.23
50 vol-% TBP + 50 vol-% MIBK	0.026 0.026 0.26 0.26	17.5 60.0 17.5 60.0	0.61 0.20 0.50 0.20
50 vol-% TBP + 50 vol-% Shellsol H	0.026 0.026 0.26 0.26	17.5 60.0 17.5 60.0	0.43 0.10 0.33 0.10
50 vol-% TBP + 50 vol-% Shellsol H	0.21	20.6	0.32
25 vol-% TBP + 75 vol-% Shellsol H	0.21	20.6	0.06
50 vol-% TBP + 50 vol-% Shellsol A	0.026 0.026 0.26 0.26	17.5 60.0 17.5 60.0	0.36 0.09 0.31 0.09
50 vol-% tri-iso-octyl amine + 50 vol-% Shellsol H	0.486	25.0	6.5
50 vol-% tri-iso-octyl amine + 50 vol-% Shellsol H	0.486	80.0	0.33

TABLE 3

Distribution coefficients for the extraction of citric acid from water solutions to an organic solvent

FIG. 1

Equilibrium curves for the extraction system
Water-Citric acid - 75 vol-% TBP in Shellsol A



The results of calculations for one case using the McCabe Thiele method and fixed concentrations in the feed, raffinate and recirculated solvent are shown in figure 2. Experiments for determining equilibrium data were made using an AKUFVE-equipment (8).

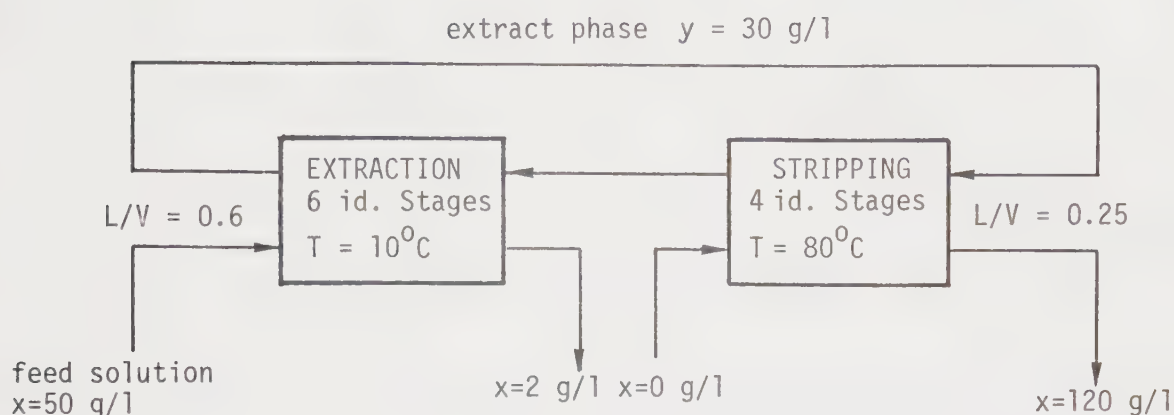


FIG. 2

Results from calculations using the McCabe Thiele method

Experimental runs in small laboratory mixer-settlers gave results in good agreement with calculations. The intention was then to carry out similar runs using a feed solution obtained by fermentation of a residual solution from an industrial process. In addition to citric acid (50 g/l), this solution contained proteins, fats, vitamins, salts etc. These components may change the distribution of citric acid and, as it turned out, greatly affected the phase separation properties. The surfactants stabilize the emulsion obtained in the mixer in such a way that the settlers flooded in spite of very low throughputs. Substances such as lecithin can increase the coalescence rate, but this can hardly be done on an industrial scale.

Tests were also carried out in a pulsed column (height 3 m, diameter 50 mm). The water phase was kept continuous, but when the phase ratio V/L exceeded 1.4 phase inversion occurred and the column flooded. It was not possible to run the column with the water dispersed. When the phase ratio was lower than 1.4 the concentration of citric acid in the raffinate phase could not be reduced below 15 g/l (the temperature was kept at 20°C and the concentration of citric acid in the feed was 37 g/l).

With this feed, the only way to carry out mixing and phase separation successfully was to use some kind of centrifugal equipment. Runs were therefore performed in a 3 stage mixer-settler battery using small Alfa Laval centrifuges as settlers. Some results from these runs are given in table 4. The solvent in this case was 70 vol-% TBP dissolved in Shellsol H.

Phase ratio V/L	Concentration in leaving raffinate, g/l
0.63	18.3
1.18	12.7

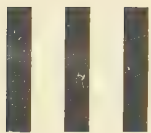
TABLE 4

Results from runs in mixer-settlers with centrifuges as settlers
(Temperature: 22°C, Feed conc.: 37 g/l)

Lowering the temperature would make it possible to use centrifugal extractors type Alfa Laval ABE 216 to carry out the extraction. The process economy is however uncertain and the present work is therefore concentrated on improving the coalescence in order to be able to use ordinary gravity settlers for the phase separation.

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THE EXTRACTION OF CITRIC ACID FROM
FERMENTATION BROTH USING A SOLUTION
OF A TERTIARY AMINE

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SUMMARY

Tertiary amines are effective extractants for citric acid. The effect of diluents on the extraction has been thoroughly investigated. It can be concluded that the diluent is very important since it affects the distribution of citric acid, the selectivity and the phase separation properties. The distribution coefficient for citric acid is strongly temperature dependent. This makes it possible to strip the acid into water at a higher temperature. Alamine 336 dissolved in a nonpolar diluent is a very suitable solvent. Pilot plant runs show that the process is technically feasible. Some new equipment has been developed for the stripping stage.

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1. INTRODUCTION

Microbiological processes have already achieved considerable industrial importance; present intensive research gives reason to expect that they will become even more important in the near future. As supplies of oil and natural gas become exhausted, it can be expected that so-called "regenerative" vegetable raw materials and their microbiological conversion will in many cases become economic in not too distant future.

An important step in such processes is the recovery of the product from the fermentation broth. The culture suspensions to be processed are not always easy to handle as they are often mixtures of micro-organisms, products and undesirable by-products or additives. There is often a high degree of flowsheet integration between concentrating and purifying steps in these processes. In view of the large number of methods which are available for recovery, the selection of the optimal method calls for experience and careful testing. Application of a sequence of unit operations without changing the aggregate state of the product, for example by using liquid-liquid extraction as the purification step instead of precipitation, gives lower production costs since intermediate isolation of a solid phase and its repeated dissolution are thereby eliminated.

The present study is a continuation of an earlier work (1) on the use of solvent extraction as an alternative to precipitation for the recovery of citric acid from aqueous fermentation solutions. Solvent screening in this earlier study was focused on the phosphoryl extractants. The main objective of the present work has been to investigate the technical feasibility of an extraction process in which citric acid is extracted from a fermentation broth using a tertiary amine dissolved in an appropriate diluent as solvent. The acid is stripped by water at a higher temperature. Although the results apply to citric acid, the process can probably, with small modifications, be applied to other organic acids.

2. AMINES AS EXTRACTANTS FOR ORGANIC ACIDS

Smith and Page (2) were among the first to report on the use of acid binding properties of long-chain aliphatic amines as extraction solvents. The extraction mechanism is an acid-base neutralization. Acid in the aqueous phase transfers to the solvent phase, where it forms a complex with the amine. If the amine is sufficiently water-insoluble, the reaction complex, stays almost entirely in the solvent phase:



where HA is the acid and B the amine.

The complex is usually termed a salt or an ion pair or a salt.

Smith and Page concluded that tertiary amines are much more efficient acid binders than primary and secondary amines. The acid-binding properties of tertiary amines improve as the length of the carbon chain increases. As molecular weight continues to increase, a maximum is reached and the optimum range seems to be amines containing eight to ten carbon atoms in the three alkyl chains. Ricker and King (3) found that a secondary amine gave a higher distribution coefficient than tertiary amines for the extraction of acetic acid. Tertiary amines are however more stable than both primary and secondary amines and are therefore preferable for use on an industrial scale. As will be shown later there is no gain in using solvents with K_D -values higher than 10 especially where, as in the present case, the acid is to be stripped by water.

The solubility of the amine and the amine-acid complex in the raffinate phase is an important factor affecting the loss of solvent and the residual concentration of solvent in the product. The water solubility of the major components of Alamine 336, a $\text{C}_8\text{-C}_{10}$ tertiary amine, is reported to be less than 5 ppm (4). Chromatographic analysis showed (3) that even in the presence of 10 wt % acetic acid, the combined solubility of these components was less than 10 ppm. However, as pointed out in the product literature of several amine manufacturers, commercial grades of these extractants contain around 2-5 wt % impurities. These can be primary and secondary amines, lower molecular weight tertiary amines, and starting materials for the amine synthesis reaction. Some of these may be quite water-soluble.

Compared to tri-butyl phosphate the tertiary amines are probably more stable and certainly less water-soluble. In this work three tertiary amines were investigated namely tribenzylamine (Merck, for synthesis), tri-dodecyl amine (Merck, for synthesis) and Alamine 336 (Henkel LTD). The main constituent in Alamine 336 is tri-n-octyl amine.

3. SOLVENT SELECTION

3.1 EFFECT OF DILUENT, AMINE STRUCTURE, TEMPERATURE, AMINE- AND ACID CONCENTRATION

In order to modify its physical properties, such as viscosity and density, the amine is usually dissolved in an organic diluent. As will be shown, the choice of diluent is a crucial step which can affect the process in many ways.

Tables 1 and 2 give distribution coefficients, K_D -values, for the extraction of citric acid with Alamine 336 and tri-dodecyl amine dissolved in different diluents, as function of acid concentration and temperature. These K_D -values were determined by equilibrating the phases in a shake-bath for twelve hours and then allowing them to settle for twelve hours. Samples were then taken from the aqueous phases and titrated with sodium hydroxide. A material balance gave the concentration in the organic layer. To check the validity of the material balance some samples were also taken from the organic phase. The samples were washed with a known, excess amount of sodium hydroxide and the excess base was then titrated with hydrochloric acid. The error was found to be less than 5 %.

As can be seen from tables 1 and 2, there is a strong effect of diluent type upon the K_D -values especially in the low acid concentration region where the complex-diluent interactions appears to have a dominant effect. The K_D -value is clearly a function of the polarity of the diluent and of its ability to form hydrogen bonds, as expressed by the solubility parameters given by Hansen (5). At higher acid concentrations, however, there is little difference in K_D -value between the diluents. The degree of complexing at any point depends on the equilibrium constant of the acid base complex formation and of the activities of the reactants and products. When the amine is highly complexed, the extraction behaviour resembles that of a non- chemical extractant, and the K_D -value is no longer a strong function of acid concentration. From these tables, it is

also clear that complex formation is strongly dependent on temperature. This parameter is important since the aim is to strip the acid into water and this can be done at a higher temperature where the distribution favours the aqueous phase. There is no great difference between tri-dodecyl amine and Alamine 336 in the effect of temperature and there will probably be even less effect of temperature if commercially-grade tri-dodecyl amine (Alamine 304) is used since these grades are often a mixture of amines. Reported prices (from Henkel, Ireland) for 5 m³ batches are 3.87 US /kg for Alamine 336 and 3.72 US /kg for Alamine 304.

Tribenzylamine was tested because of its low extraction capacity for sulphuric acid (6) which is present in small amounts in the fermentation solutions. Experiments showed however that the K_D -value was almost zero for citric acid as well. As Alamine 336 was available it was selected for further studies. The distribution coefficients in the region with high acid concentration do not differ very much between the diluents. The lowest value in the dilute region is 2.9. It can therefore be concluded from McCabe-Thiele stage-calculations (table 3) that not much is gained by choosing a diluent giving a K_D -value greater than 10 in the diluted region. Stripping must also be taken into consideration and here a low K_D -value is desirable. There are also several other advantages in using a rather non-polar diluent in the process as will be shown later. Nitrobenzene and chlorinated hydrocarbons are unsuitable because of their density and potential toxicity. Tables 4 and 5 give equilibrium data for the system water - citric acid - Alamine 336 + diluent at two different temperatures. The diluents are isopar H (a paraffinic kerosene), isopar H + methyl-iso-butyl ketone and butyl chloride. The later was chosen since it was the only chlorinated hydrocarbon with a density less than one. For all curves there is a maximum value at an intermediate concentration. The theoretical molecular weight of Alamine 336 is 353 kg/kmol and this would give a concentration of amine in the solvent phase of about 1 M. The maximum is reached when the concentration in the organic phase is 0.3-0.4 M. Since citric acid has three carboxyl groups, it seems logical to assume that the amine is saturated with citric acid at the maximum and that further acid is extracted as "excess" acid.

3.2 THIRD PHASE FORMATION

If a concentration region is reached where excess citric acid is extracted, there is a tendency for the formation of a third phase in the organic phase. The amine itself is a poor solvent for the complex and there will therefore be two organic layers if the acid concentration is high and no diluent is used. The upper organic layer will consist mainly of amine and the lower of the acid-amine complex. The effect of the diluent on the formation of a third phase was therefore investigated. A solution containing 0.83 M citric acid (this is the maximum concentration which can be obtained in the broth) was extracted with an organic phase consisting of Alamine 336 dissolved in different diluents. The phases were allowed to settle and the organic phase was observed. The results are given in Table 6. The third phase which was formed when the solubility of the complex in the amine-diluent was exceeded was extremely viscous and the acid could not be stripped by water even when a high temperature was used. This indicates that the formation of a third phase must be avoided in an industrial process. It is clear that if an excess of a non-polar diluent is used, the concentration of the complex in the organic phase must be kept low by using a high phase ratio, V/L, in the extractor.

3.3 SELECTIVITY

The fermentation broth contains a range of impurities. Many of these are dark in colour and have a mean viscosity of 2.4 cP at 25°C. There are also raw material and micro-organism residuals present as solids. The moulds are grown on pellets which are about five millimeter in diameter and have a density greater than one. The solution used in the experiments was screened, to filter off the pellets. This broth was extracted by solvents of different composition and the colour of the organic phase and the phase separation were observed. From the results shown in Table 7 it is clear that the best selectivity and the best phase separation is obtained using a non-polar diluent like n-hexane.

3.4 CHOICE OF DILUENT

The choice of a proper diluent for the amine is not an easy task. There are several important parameters which must be taken into account. The most important are discussed below.

Distribution coefficient: The K_D -value in the extraction step should be greater than 1 at room temperature and below 0.1 in the stripping step in order to obtain a high concentration in the stripping raffinate.

Selectivity: It is important that as little of the impurities as possible is extracted since these can build up in the organic phase or turn up in the raffinate phase after stripping. This favours a non-polar diluent.

Toxicity: It is difficult to estimate this parameter since the regulations are diffuse. There are two points to consider: the regulations for residual chemicals in the product and the concentrations tolerable in air and in the raffinate phase. A long-chain paraffinic hydrocarbon seems to offer the most promising characteristics for the process under consideration. These have low solubility in water and are probably removed from the aqueous phase during evaporation.

Low solubility in water: This is important for several reasons. One is of course economy if the diluent has to be recovered from the raffinate phase by stripping or if it is lost. The physical properties of the fermentation broth make it desirable to avoid raffinate stripping. Since the raffinate will be fed to a methane production plant a low concentration of some cheap hydrocarbon can be tolerated.

Viscosity and density: Low viscosity and density promote phase separation. These properties are optimal with paraffinic hydrocarbons.

Stability: Hydrocarbons must be preferred to alcohols and halogenated hydrocarbons.

3.5 CONCLUSIONS

Tertiary, aliphatic amines with approximately eight carbon atoms in each alkyl group have excellent potential for the extraction of citric acid. Among the diluents, the hydrocarbons seem to offer the most promising characteristics for this specific process. The main disadvantage of these diluents is however their low capacity. This can be overcome by keeping a high phase ratio in the extraction stage so that third phase formation is avoided. The aromatic hydrocarbons have a greater solvency for the amine-acid complex than the paraffinic. The choice of phase continuity also affects the choice of phase ratio unless recirculation of one phase is adopted. Runs in small glass mixer-settlers where the flows were stopped during the run and the coalescence rate observed, indicated that the aqueous phase should be kept dispersed. The separation of micro-organisms from the culture suspension is a difficult operation. This favours direct extraction of a fermentation broth containing pellets. If this is done, the organic phase must be continuous since there is a residue of citric acid within the pellets.

4. EXTRACTOR SELECTION AND PILOT PLANT RUNS

As the filtration of the fermentation broth is a difficult operation there is a great incentive for direct extraction without feed treatment. In stage-wise equipment such as mixer-settlers it is difficult to handle the transport of the solid pellets if more than one stage is needed. In the pump-mix mixer-settler there is also a risk that the agitation will be too violent since the surface tension between the phases is small. Among differential equipment, centrifugal extractors are too expensive since the product value is low. In this case the solid content in the feed will more over give arise to severe problems. If a column is to be used it must be agitated in some way to ensure enough theoretical stages. The free area in the column must allow for the throughput of the pellets. With these restrictions some kind of rotating disc column or a Karr column may be appropriate. Some arrangement must be provided to control the velocity of the pellets through the column and to withdraw the pellets from the bottom. The Karr reciprocating column was successfully used by Karr et al (7) for the extraction of penicillin from whole fermentation broth. The uncertainties in the extraction process will be the mass transfer and phase separation properties since the feed contains surfactants and solid particles. As shown by Wennersten (8) these problems can to some degree be overcome by a proper choice of diluent. The particles in the feed will tend to place themselves where the energy of the system is at a minimum. Thus the surface energy between the particles and the solvent is a variable which can be used to minimise these problems.

In order to quantify the difficulties in operating a column, an existing pulsed plate column was fed with screened fermentation broth. The solvent phase consisted of 30 vol % Alamine 336 dissolved in 70 vol % Shellsol A, a kerosene with a high aromatic content. Equilibrium curves for this system with the amine concentration as parameter are given in figure 1. Results from a run are shown in table 8 together with the column specifications. Experience from these runs, and from earlier runs using TBP dissolved in kerosene, indicates that startup problems can arise. The column was filled with organic phase before the feed was introduced. The phase ratio V/L was 2.0 to assure that the aqueous phase be dispersed. From the beginning an aggregate consisting of organic phase and a small amount of solids quickly filled almost the entire length of the column. The aggregate left the column at the top and filled the separation vessel. After two hours the interface between the aggregate and the working part of the column began to move upward and after about four hours the column

worked perfectly. The organic phase leaving at the top was clear with no content of solids. In the separation vessel at the bottom of the column there was no dispersion band or sign of crud formation. Under these conditions the column was run for about ten hours. The starting up problems can probably be reduced if the organic phase is conditioned before entering the column.

The stripping should be carried out at an elevated temperature in order to obtain a high concentration of citric acid in the raffinate phase. In figure 2 the temperature dependence of K_D for the solvent (Alamine 336 dissolved i 50 vol % Shellsol A) clearly indicates the potential value of high temperatures in the stripper. These K_D -values were obtained with the equipment seen on figure 3. If the temperature is higher than 100°C, which is desirable, it will be difficult to carry out the mixing and separation in an ordinary extraction equipment.

A new technique was therefore tested in which an Alfa-Laval plate heat exchanger is used as a static mixer and heater at the same time. The heat exchanger, which is of the type P01, was equipped with 28 corrugated plates arranged in such a way that the two phase mixture passed the plates in series while the heating medium, which was water, passed in parallell. Before entering the heat exchanger the water was dispersed in the solvent through an Alfa-Laval sterilizing nozzle (figure 4). The solvent flow rate was 1.2 l/min and the flow of water for stripping was 0.4 l/min. The residence time in the stripping section was 40 seconds. The calculated Reynolds number indicated that the two-phase flow was turbulent. In this run the temperature was kept at 63°C and the extractor had the equivalent of almost one theoretical stage. With this arrangement, it will be easy to use steam as heating medium thus reducing the K_D -value considerably. The phases were separated efficiently in a Quickfit pipe used as settler in a Quickfit mixer-settler. If one such stage is used for stripping it is possible to use another stage working at a higher temperature to wash the organic phase before it is returned to the extraction column.

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Table 1: Effect of diluent on the extraction of citric acid with Alamine 336.
Ratio of amine/diluent = 1.0 (vol.)

Solvent	Temperature (°C)	Conc. of citric acid in raffinate phase (M)	K_D	Solubility parameters		
				σ_D	σ_P	σ_H
Alamine 336 + n-hexane	25	$14.3 \cdot 10^{-3}$	2.9	7.3	0	0
"	25	0.382	1.9			
"	60	$37.9 \cdot 10^{-3}$	0.3			
Alamine 336 + toluene	25	$4.93 \cdot 10^{-3}$	10.8	8.8	0.7	1.0
"	25	0.358	2.1			
"	60	$22.1 \cdot 10^{-3}$	1.4			
Alamine 336 + 1,1,1-trichloroethane	25	$3.37 \cdot 10^{-3}$	16.4	8.3	2.1	1.0
"	25	0.348	2.2			
"	60	$12.5 \cdot 10^{-3}$	3.5			
Alamine 336 + ethyl acetate	25	$2.45 \cdot 10^{-3}$	23.0	7.7	2.6	3.5
"	25	0.275	3.1			
"	60	$15.7 \cdot 10^{-3}$	2.5			
Alamine 336 + MIBK	25	$2.07 \cdot 10^{-3}$	27.5	7.5	3.0	2.0
"	25	0.276	3.1			
"	60	$5.17 \cdot 10^{-3}$	11.5			

Table 1: continued

Alamine 336 + cyclohexanone	25	$1.87 \cdot 10^{-3}$	30.5 (25)	8.7	3.1	2.5
"-	25	0.220	4.2			
"-	60	$3.2 \cdot 10^{-3}$	17.3			
Alamine 336 + 2-ethylhexanol	25	$0.83 \cdot 10^{-3}$	70.0	8.3	1.6	5.8
"-	25	0.351	2.1			
"-	60	$1.97 \cdot 10^{-3}$	28.9			
Alamine 336 + iso-amyl alcohol	25	$0.67 \cdot 10^{-3}$	87.8		not available	
"-	25	0.305	2.7			
"-	60	$1.37 \cdot 10^{-3}$	42.2			
Alamine 336 + dichlor methane	25	$0.63 \cdot 10^{-3}$	92.4	8.9	3.1	2.0
"-	25	0.372	2.0			
"-	60	$6.33 \cdot 10^{-3}$	8.1			
Alamine 336 + nitrobenzene	25	$0.60 \cdot 10^{-3}$	97.6	9.8	4.2	2.0
"-	25	0.340	2.2			
"-	60	$1.76 \cdot 10^{-3}$	32.3			
Alamine 336 + n-butanol	25	$0.35 \cdot 10^{-3}$	168.3	7.8	2.8	7.7
"-	25	0.274	3.1			
"-	60	$0.80 \cdot 10^{-3}$	72.9			

Table 2: Effect of diluent on the extraction of citric acid with tri-dodecyl amine

1 M of amine dissolved in diluent

Diluent	Temperature (°C)	Conc. of citric acid in raffinate phase (M)•10 ³	K _D
MIBK	25	1.70	34
—"	60	9.87	4.8
2-Ethylhexanol	25	0.33	177
—"	60	1.80	31.7
Toluene	25	8.20	6.0
—"	60	329	0.55
Chloroform	25	0.43	136
—"	60	3.13	17.7

Table 3: Effect of diluent on number of theoretical stages

Solvent: 50 vol % Alamine 336 + 50 vol % diluent

Temperature: 25°C

Phase ratio V/L = 1.0

Concentration of citric acid in feed = 0.7 M

Concentration of citric acid in outgoing raffinate = 0.02 M

Concentration of citric acid in incoming organic phase = 0.02 M

Diluent	Number of theoretical stages
n-Butanol	1.9
Toluene	2.9
n-Hexane	4.0

Table 4: Effect of diluent and acid concentration on the extraction of citric acid with Alamine 336

Temperature = 25°C

Solvent	Conc. of citric acid in aqueous phase at eq. (M)	K_D
Alamine 336 + Iospar H (1:1)	0.0110	4.15
	0.0109	4.22
	0.0197	7.97
	0.0280	9.60
	0.0677	7.99
	0.128	4.75
	0.193	3.48
	0.295	2.34
	0.390	1.85
	0.621	1.19
	1.000	0.76
Alamine 336 + Isopar H + MIBK (2:1:1)	0.0042	13.0
	0.0067	25.9
	0.0077	38.4
	0.0227	26.3
	0.062	11.1
	0.128	5.90
	0.230	3.36
	0.323	2.50
	0.565	1.44
	0.954	0.86
Alamine 336 + n-butyl chloride (1:1)	0.0043	12.5
	0.0062	27.8
	0.0087	33.8
	0.0273	21.6
	0.075	8.97
	0.151	4.81
	0.258	2.86
	0.357	2.13
	0.597	1.29
	1.001	0.76

Table 5: Effect of diluent and acid concentration on the extraction of citric acid with Alamine 336

Temperature = 60°C

Solvent	Conc. of citric acid in aqueous phase at eq. (M)	K_D
Alamine 336 + Isopar H (1:1)	0.0887	0.79
	0.125	1.17
	0.201	1.86
	0.272	1.57
	0.331	1.51
	0.415	1.30
	0.497	1.18
	0.700	0.92
	1.067	0.63
Alamine 336 + Isopar H + MIBK (2:1:1)	0.0280	5.22
	0.793	6.63
	0.186	3.65
	0.369	2.03
	0.600	1.28
	0.982	0.80
Alamine 336 + n-butyl chloride (1:1)	0.0163	2.40
	0.0341	4.06
	0.0455	5.42
	0.0937	5.42
	0.146	4.00
	0.213	3.04
	0.312	2.14
	0.405	1.74
	0.636	1.13
	1.027	0.71

Table 6: Studies of third phase formation

Aqueous phase: 0.83 M citric acid

Organic phase: Alamine 336 + 50 vol % diluent

Diluent	Third phase	Viscosity cP
no diluent	+	
25 ml Isopar H + 0 ml toluene	+	
20 "- + 5 "-	+	
15 "- + 10 "-	+	
10 "- + 15 "-	-	
5 "- + 20 "-	-	34.0
20 ml Isopar H + 5 ml MIBK	+	
15 "- + 10 "-	-	
0 "- + 25 "-	-	16.4
25 ml Shellsol A	-	41.1

+ third phase was formed

- third phase was not formed

Table 7: Selectivity and phase separation properties

Procedure: 15 ml fermentation solution + 30 ml solvent was shaken for 30 s and then allowed to separate.

Solvent	Colour of extract phase	Phase separation rate
Alamine 336	yellow	moderate
2-Ethylhexanol	brown	moderate
n-Butyl chloride	brown	slow
n-Hexane	uncoloured	fast
50 vol % Alamine 336 + 50 vol % 2-ethyl hexanol	yellow	slow
50 vol % Alamine 336 + 50 vol % n-hexane	slightly yellow	moderate

Table 8: Experimental run in a pulsed plate column

Solvent: 30 vol % Alamine 336 + 70 vol % Shellsol A

Flow of extract phase: 3.6 l/h

Flow of raffinate phase: 1.8 l/h

Concentration of citric acid in feed: 0.58 M

Concentration of citric acid outgoing raffinate: 0.016 M

Temperature: 25°C

Length of column: 3.0 m

Diameter: 0.05 m

Pulsation frequency: 60/min

Pulsation amplitude: 0.012 m

Fig. 1: Equilibrium curves for the system
water-citric acid-Alamine 336 + Shellsol A
Temp. = 25°C

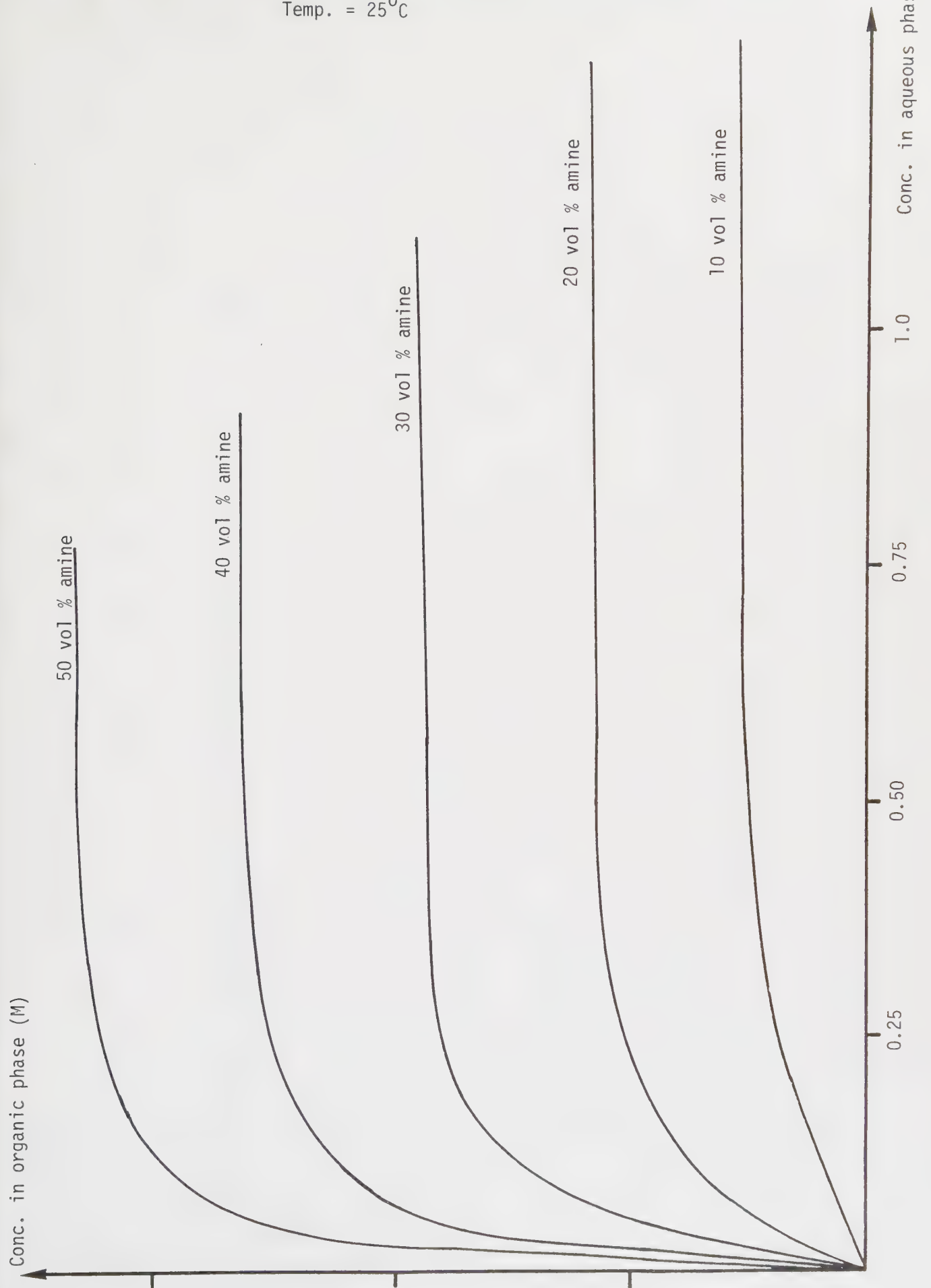


Fig. 2: Effect of temperature on K_D -value for the system
water-citric acid-50 vol % Alamine 336 + Shellsol A

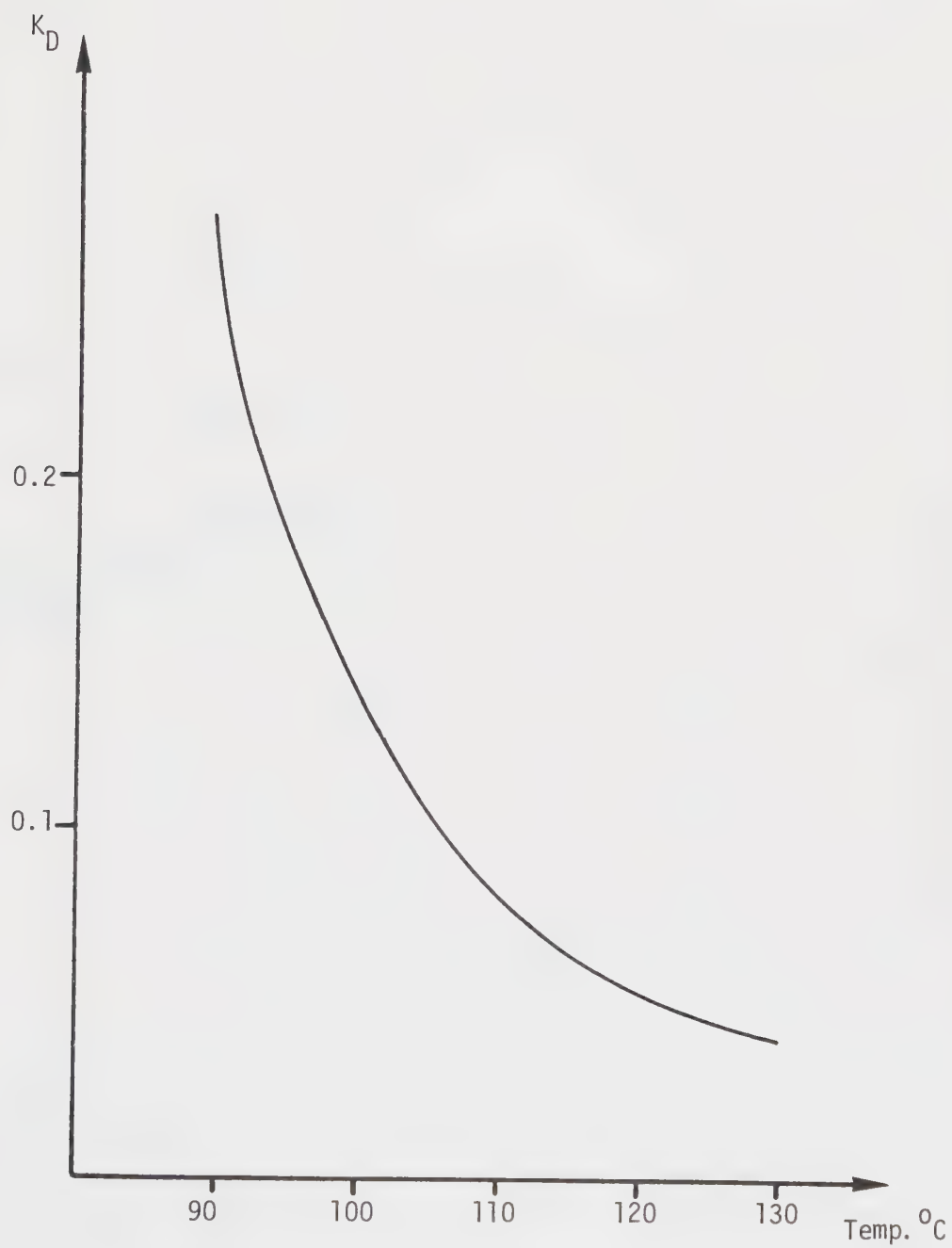
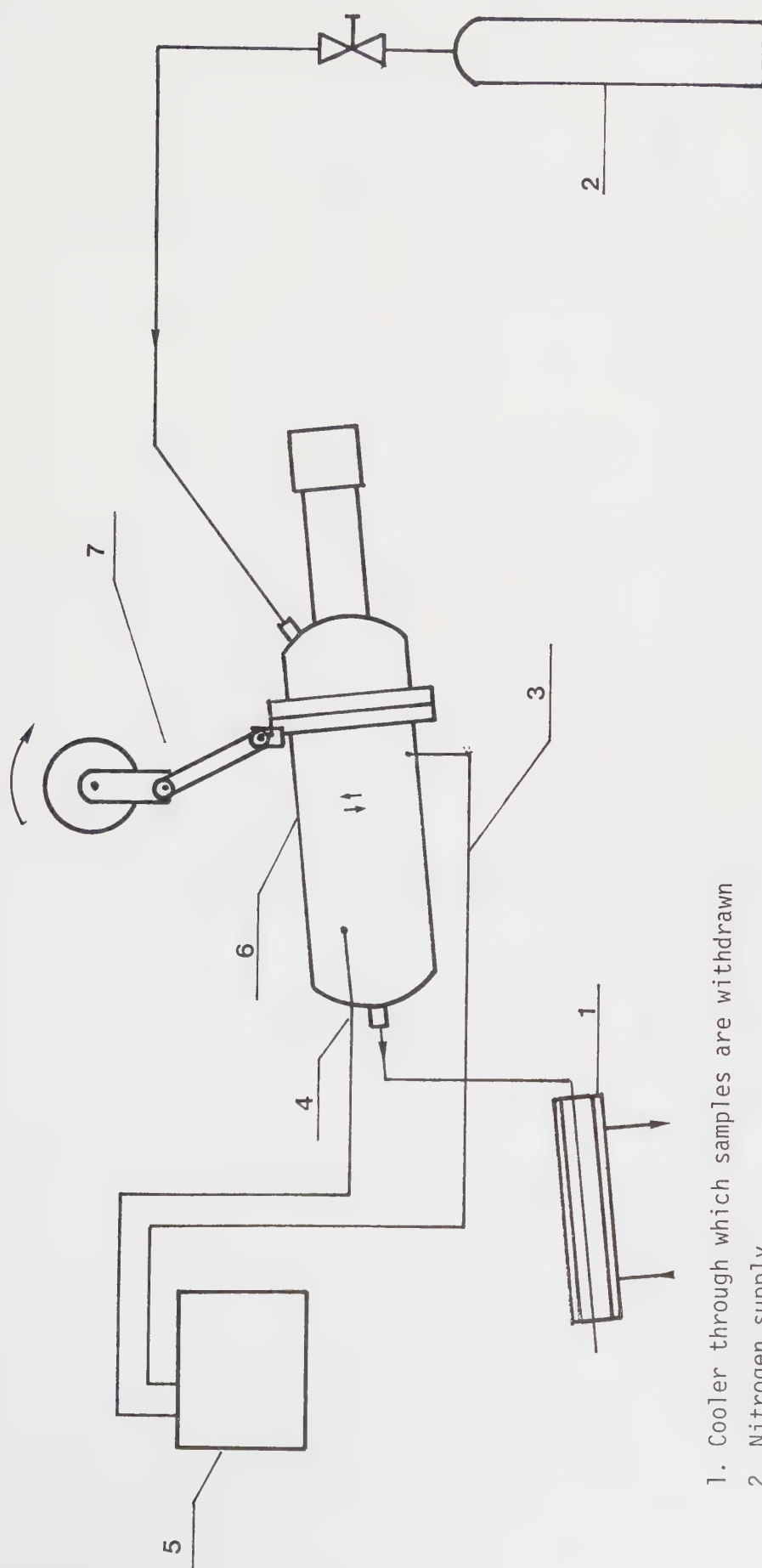
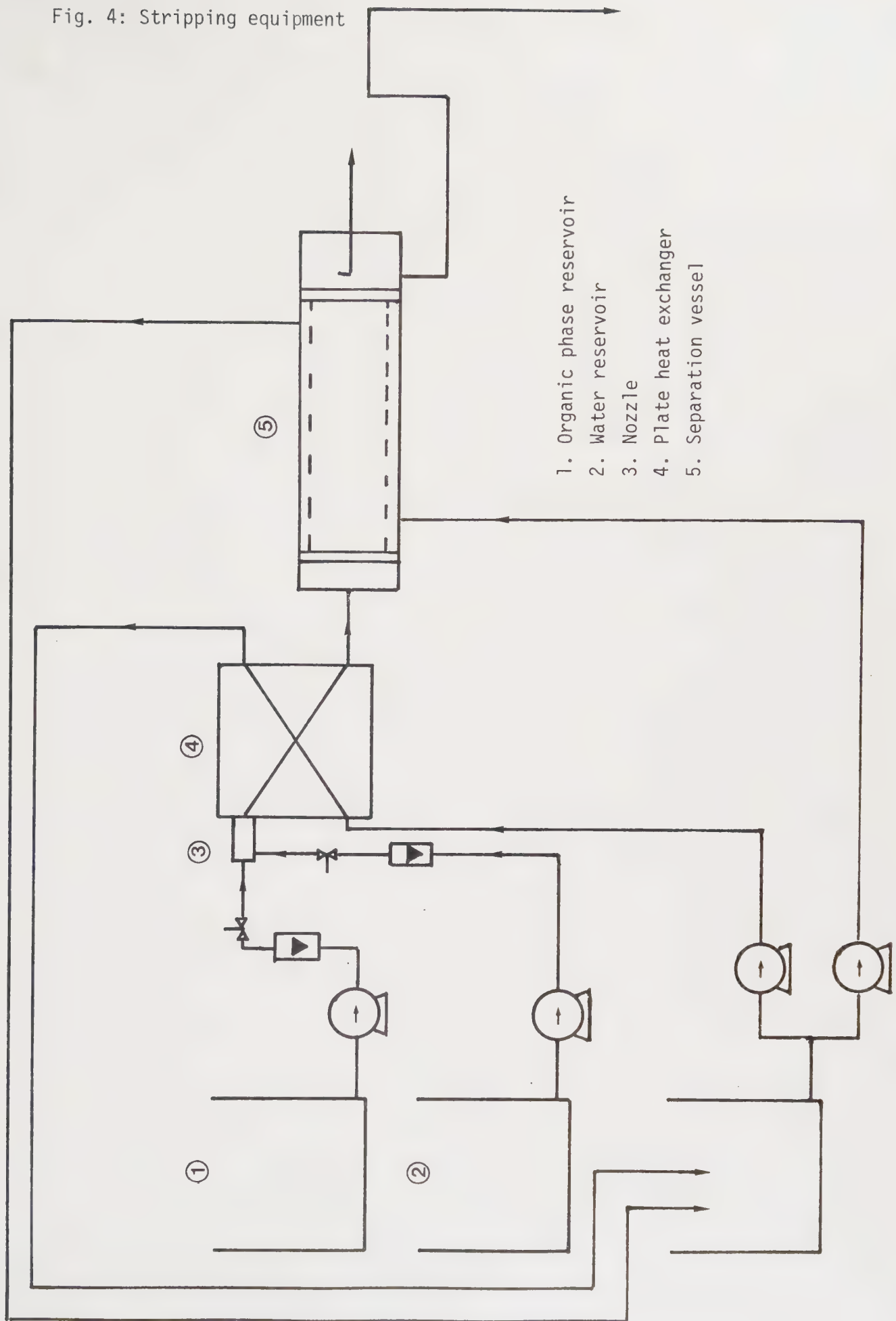


Fig. 3: Apparatus for determining distribution coefficients at high temperatures.



1. Cooler through which samples are withdrawn
2. Nitrogen supply
3. Pressure gauge
4. Thermo couple
5. Recorder
6. Extraction cell
7. Shaking mechanism

Fig. 4: Stripping equipment



A SOLVENT EXTRACTION-DISTILLATION PROCESS FOR
TREATMENT OF CONDENSATE EFFLUENTS CONTAINING
ORGANIC SUBSTANCES AND ECONOMIC RECOVERY OF BYPRODUCTS

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A SOLVENT EXTRACTION-DISTILLATION PROCESS FOR TREATMENT OF CONDENSATE EFFLUENTS CONTAINING ORGANIC SUBSTANCES AND ECONOMIC RECOVERY OF BY-PRODUCTS.

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SUMMARY

Different solvent extraction-distillation processes for treatment of sulfite pulping condensates and for economic recovery of byproducts, essentially furfural, methanol and acetic acid, were studied. The investigation was carried out in the following three steps: solvent screening based on approximative calculations of energy requirement, rigorous computer simulations and experimental investigation in labscale and pilot equipment.

The following three separation routes were studied: neutralisation of thin liquor and recovery of methanol and furfural by extraction, fractionation of methanol and furfural followed by acetic acid extraction, and simultaneous extraction of furfural and acetic acid. The best solvents investigated, as far as energy requirement is concerned, turned out to be:

- chloroform for the extraction of furfural,
- high molecular tertiary amines dissolved in high-boiling alcohols for the extraction of acetic acid and
- ethyl acetate for the simultaneous extraction

The computer programs PRIMCALC, for preliminary solvent screening, and DESTEX, for rigorous simulation of extraction-distillation processes, greatly facilitated the calculation effort in this investigation.

INTRODUCTION

The condensate effluent from bisulfite pulping contains, among other organic substances, acetic acid, methanol and furfural. Much effort has been expended in recent years to find an economical and practical means of disposing such condensates.

Baierl (1) described a method of recovering methanol and furfural from a sulfite pulp effluent by treating the effluent with steam in a fractionating column.

In an investigation supervised by Kringstad (2), it was concluded that a recovery system for furfural and acetic acid based on adsorption and distillation is uneconomic.

Baierl et al. (3) suggested a process where acetic acid was adsorbed by active carbon followed by regeneration of the carbon with ethanol yielding ethyl acetate as the product. In this process, adsorption by active carbon seems to have offered severe technical problems.

Zacchi and Aly (4) showed that by incorporating the stripper in the evaporation plant, the recovery of furfural and methanol could be achieved in an economic way.

Many authors have suggested the use of solvent extraction for the recovery of furfural, for instance Trimble and Dunlop (5), Rigamonti and Marchetti (6) and Kikic et al. (7), and acetic acid, for instance Shah and Tiwary (8), Wardell and King (9) and Ricker and King (10), from aqueous solutions. It seems that solvent extraction and distillation offer potential methods for treating sulfite condensates. One of the major objectives of this work is to design a solvent extraction-distillation process for treatment of sulfite pulping condensates and for economic recovery of by-products, essentially furfural, acetic acid and methanol.

SELECTION OF AN "OPTIMAL PROCESS"

The general process design strategy must be to find the most economic process when certain process conditions are fixed. The most important conditions are:

condensate flowrate
concentrations of byproducts
environmental and process (if recirculated) restrictions

Due to variation from one mill to another there is probably no single process which is applicable to the whole spectrum of liquors to be treated. The calculations must therefore be carried out in such a way that the economy for the most promising process design alternatives is evaluated as a function of the conditions given above.

The selection of a proper solvent is of fundamental importance since this choice determines the main feature of the process. There are several important criteria which must be taken into consideration when selecting a solvent for a specific process.

- a) Distribution coefficient and selectivity for the solute to be recovered
- b) Mutual solubility with water.
- c) Separation factors in the solvent recovery steps.
- d) Physical properties such as boiling point, density, viscosity and interfacial tension.
- e) Stability against degradation
- f) Toxicity.
- g) Price and availability.

From these criteria an "optimal process" can be designed when the feed solution is specified. The different separation routes, outlined below, were investigated using a general routine consisting of three different steps in order to select the "optimal process". The first step involves solvent screening based on simplified calculations for different solvent alternatives. These calculations are carried out using a computer program, Wennersten et al. (11), where the energy requirement in the solvent regeneration steps is compared with the amount of byproduct recovered.

In the second step the selected solvents are tested using a more rigorous computer program for extraction-distillation simulations, Zacchi and Wennersten (12). From these calculations the different processes can be optimized and compared taking into account both technical and economical aspects.

The third step involves experimental investigations in laboratory and pilot equipment in order to verify the simulations and to study parameters such as phase separation properties and solvent stability.

SEPARATION ROUTES

Three different separation routes, in which the pollutants can be removed, are outlined below.

1. NEUTRALISATION OF THIN LIQUOR AND RECOVERY OF METHANOL AND FURFURAL

The objective of neutralising thin liquor is to suppress acetic acid concentration in the condensate obtained in the evaporation process.

1a. Steam stripping followed by two fractionation columns would yield furfural and methanol.

The steam consumption in this alternative, using a two stripper configuration will be 56 tons of live steam per ton furfural recovered. A better alternative, concerning steam consumption, is to incorporate the stripper in the evaporation plant as shown by Zacchi and Aly (4).

1b. Extraction of furfural and some methanol

Furfural and some methanol can be extracted using either a low-boiling solvent, see Figure 1, or a high-boiling solvent, see Figure 2.

A detailed study of 9 solvents, including experimental determination of distribution coefficients, computer simulations and laboratory-scale experiments, was performed. Minimum steam consumption for these solvents is displayed in Figures 3 and 4.

Chloroform turned out to be the best solvent for recovery of furfural, as far as energy consumption is concerned. This is due to a high K_D -value, high relative volatility to both furfural and water, and low solubility in water. A disadvantage of chloroform is its toxicity which would require costly safety measures if used on industrial scale. A less toxic chlorinated hydrocarbon which has gained an increasing interest is 1,1,1-trichloroethane which, although not as good as chloroform, still gives a lower steam consumption than the other low-boiling solvents studied.

Tetralin turned out to be the best high-boiling solvent studied, concerning steam consumption, but it must be modified with a diluent

having a lower density in order to improve phase separation properties.

Detailed results are given by Wennersten et al (13).

2. FRACTIONATION OF METHANOL AND FURFURAL FOLLOWED BY ACETIC ACID EXTRACTION

Acetic acid will remain in the bottoms leaving the stripper and the methanol column. Solvent extraction of acetic acid followed by distillation can be employed in either two ways.

2a. Using a high-boiling solvent

Calculations of minimum steam consumption were carried out using five high-boiling solvents and are summarized in Table 1. From these calculations and from other considerations, mentioned in Wennersten et al. (14), high molecular weight tertiary amines dissolved in a proper diluent were found to offer the most economic way to recover acetic acid from dilute aqueous solutions. The amines are readily available at rather low cost on the market, they are chemically stable and the solubility in water is extremely low. The influence of the diluent was studied thoroughly as it strongly affects the process economy. Using alcohols as diluents, the highest distribution coefficients were obtained, which would result in low extract phase flows. The critical properties of the diluent, concerning steam consumption, is the solubility in the raffinate phase, the stripping factor and the relative volatility of acetic acid to the diluent-amine mixture. The selection of a diluent requires measurement of VLE-data for the systems diluent-water and acetic acid-amine-diluent.

Experimental runs were carried out where acetic acid was extracted using Alamine 336 + 50 vol % 2-ethyl hexanol as solvent. An example of such a run is given in figure 5. No dispersion band was obtained in the settler as the coalescence was rapid. The extract phase was distilled in a batch distillation unit. Analysis on gas chromatography did not give any measurable quantities of esters but some lighter components from the amine turned up in the distillate indicating impurities in the amine. Esterification thus does not seem to cause any troubles and if a small amount of ester should turn up this will probably not affect the process since the boiling point is high and the solubility in water low. Long runs must however be carried out to verify this.

2b. Using a low-boiling solvent

Of different low-boiling solvents examined, ethyl acetate was the most promising solvent. Minimum steam consumption in a process for extraction of acetic acid using ethyl acetate is given in Table 2 for different feed concentrations. Using a low-boiling solvent, the distribution coefficient value proved to be critical for steam consumption. This is because the K_D -value determines the flow of the extract phase and all solvent is taken as top product in the solvent recovery column, see figure 1. Steam consumption using ethyl acetate is higher than that using the best high-boiling solvent but is still favourable compared to distillation of diluted acetic acid solutions. An advantage for the low-boiling solvent is that no high boiling substances can accumulate in the solvent. The phase separation properties when using ethyl acetate are also very good.

3. SIMULTANEOUS EXTRACTION OF FURFURAL AND ACETIC ACID

A solvent which will extract furfural and acetic acid simultaneously from a water solution has to fulfill several requirements beside the general ones mentioned earlier. One important restriction is that no azeotropes should be formed with the solutes which are to be recovered.

3.a Using a low-boiling solvent

Among the low-boiling solvent studied, it is obvious that ethyl acetate is the solvent which gives the lowest steam consumption. Butyl acetate is more stable concerning the hydrolysis of the ester, but due to low K_D -values, it will not be competitive.

To test the stability of ethyl acetate, this solvent was contacted with a water solution containing methanol (5 g/l), furfural (1 g/l) and acetic acid (10 g/l). The extract phase was distilled at atmospheric pressure in a batch distillation unit with total reflux for 10 hours. The solution was then analysed on gas chromatography and no traces of ethanol or methyl acetate could be found.

3b. Using a high-boiling solvent

According to the above mentioned studies of acetic acid extraction, the best solvents selected were either amines or phosphoryl reagents.

The diluent should be able to solve the amine-acid complex and at the same time capable of extracting furfural in order to avoid an additional solvent.

The diluent ought to be a high-boiling so that one does not end up with a distillation of furfural from pure amine or phosphoryl reagent, since the later components are very high-boiling.

As alcohols form azeotropes with the alcohols of interest (6), the high-boiling diluents isophorone and tetralin were selected for further investigations. These diluents extract furfural and can extract acetic acid to a sufficient degree when mixed with either an amine or a phosphoryl reagent. However, the tests carried out showed that the phase separation properties were very poor for these mixtures.

From the investigations carried out in this separation route, ethyl acetate turned out to be the only solvent which could extract furfural and acetic acid simultaneously in an economic way compared to the previous separation routes for separate removal of furfural and acetic acid. A suggested process scheme for extraction with ethyl acetate is shown in Figure 6. Energy requirement in this case will be equal to that for separation route 2b plus the energy needed to separate acetic acid from furfural in the product separation column shown in figure 6. The latter energy requirement fraction is, however, negligible.

Further long-run pilot plant studies must be carried out in order to study solvent stability, phase separation properties and the effect of accumulation of lower-boiling substances such as methanol in the overhead stream of the raffinate stripper.

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TABLE 1: MINIMUM STEAM CONSUMPTION IN A PROCESS FOR EXTRACTION OF ACETIC ACID USING DIFFERENT SOLVENTS

SOLVENT	CONC. OF C IN FEED G/L	TONS OF STEAM/H USED IN THE SEPARATION OF			STRIPPING OF RAFFINATE (TONS OF STEAM/H)	TONS OF STEAM/ TON ACETIC ACID RECOVERED
		A FROM (B+C)	C FROM B	A FROM C		
CYCLOHEXANONE	5	0.109	0.038	0.243	0.043	107.5
	10	0.109	0.038	0.303	0.043	54.8
	15	0.109	0.038	0.313	0.043	37.3
FURFURAL	5	0.123	0.090	0.181	0.23	138.3
	10	0.123	0.089	0.278	0.23	78.9
2-ETHYL HEXANOL	5	0.058	0.086	0.172	0.005	71.4
	10	0.058	0.086	0.191	0.005	25.2
TOPO+2-HEPTANONE	5	0.012	0.083	0.035	0.005	30.0
	10	0.012	0.084	0.035	0.005	15.4
	15	0.012	0.083	0.036	0.005	10.1
ALAMINE 336 +	5	0.007	0.011	0.025	0.005	10.6
2-ETHYL HEXANOL	10	0.007	0.011	0.025	0.005	5.3
	15	0.007	0.010	0.025	0.005	3.6

A = WATER
B = SOLVENT
C = ACETIC ACID

TABLE 2: MINIMUM STEAM CONSUMPTION IN A PROCESS FOR EXTRACTION OF ACETIC ACID USING ETHYL ACETATE

SOLVENT	CONC. OF ACID IN FEED G/L	SEP. OF WATER AND ACETATE FROM ACID (TONS OF STEAM/H)	STRIPPING OF RAFFINATE (TONS OF STEAM/H)	TONS OF STEAM/TON ACID RECOVERED
ETHYL ACETATE	5	0.283	0.021	67.5
	10	0.282	0.021	33.7
	15	0.282	0.021	22.4

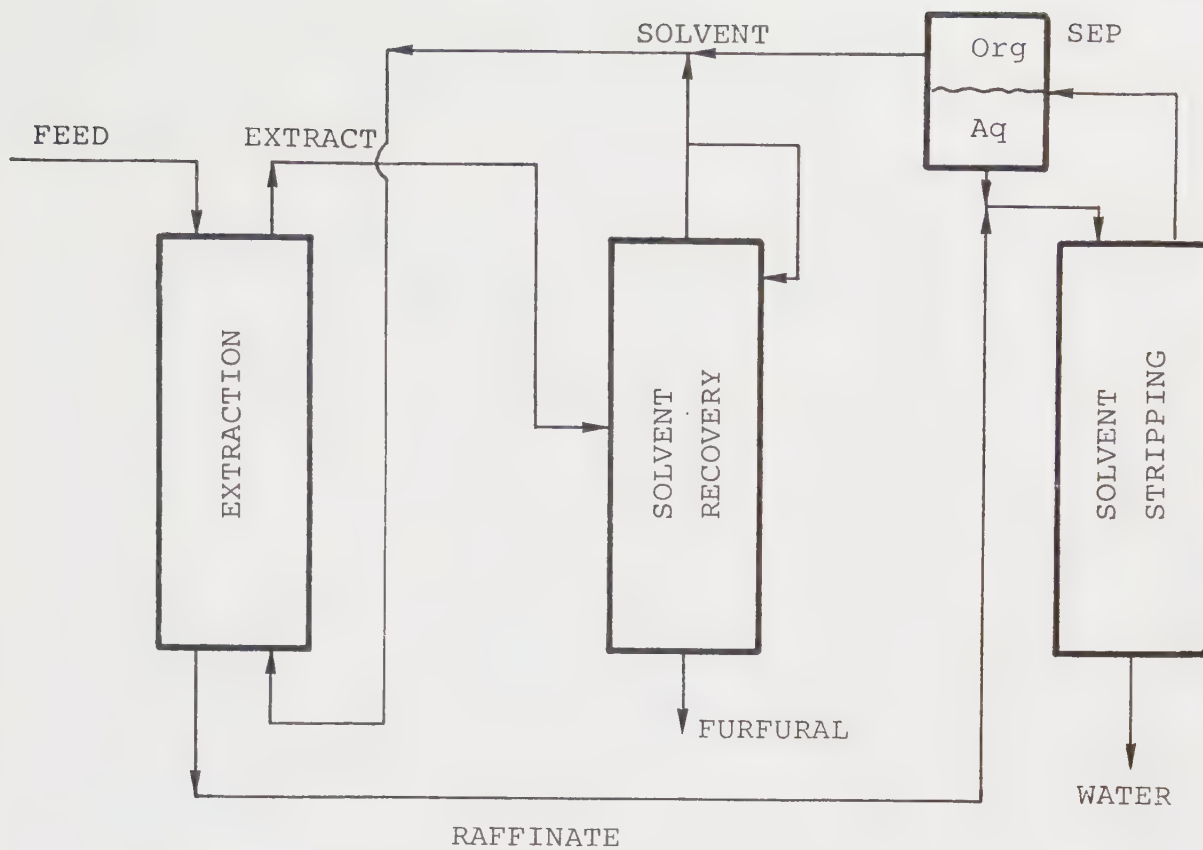


FIGURE 1: EXTRACTION OF FURFURAL WITH LOW-BOILING SOLVENTS

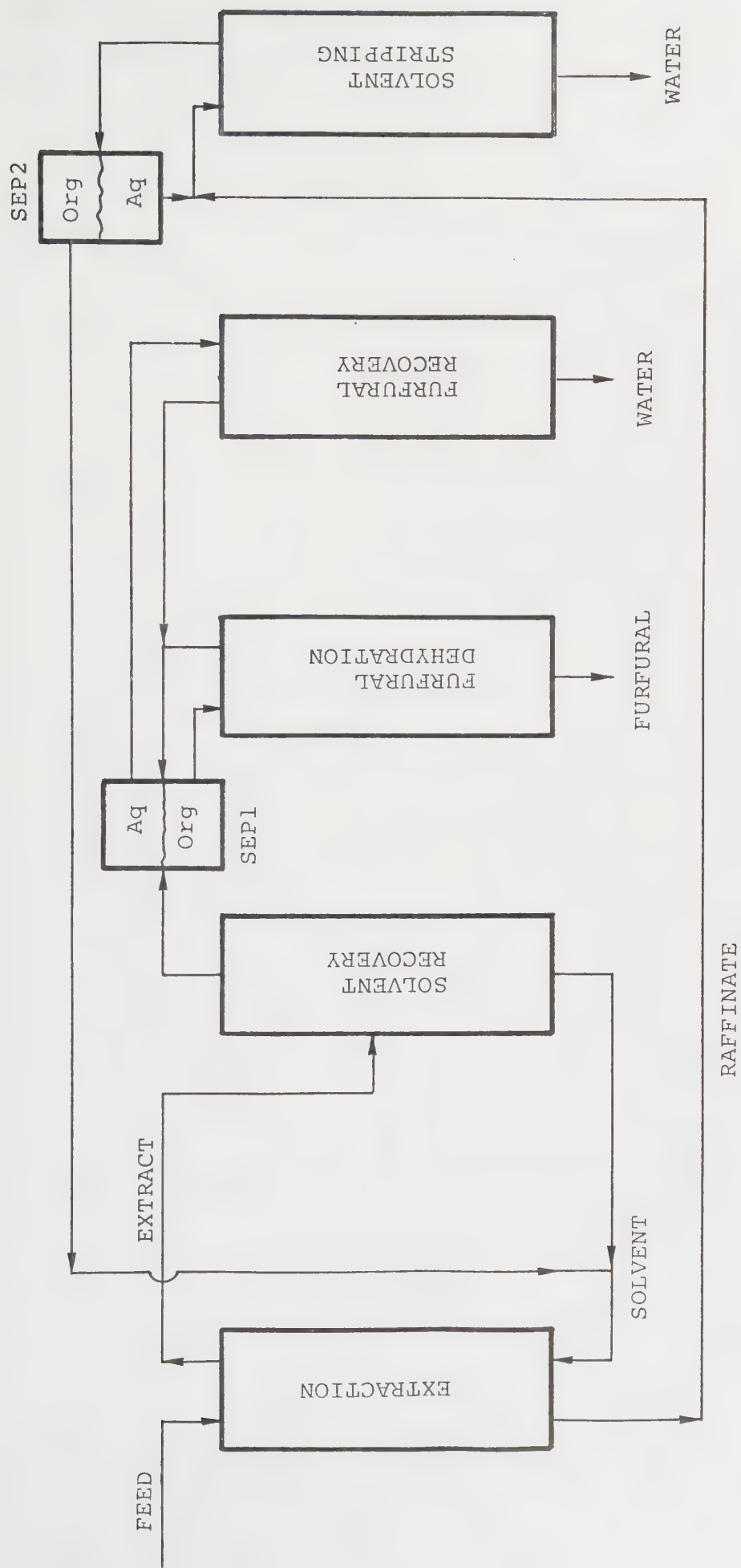


FIGURE 2: EXTRACTION OF FURFURAL WITH HIGH-BOILING SOLVENTS

STEAM CONSUMPTION
(ton/ton furfural)

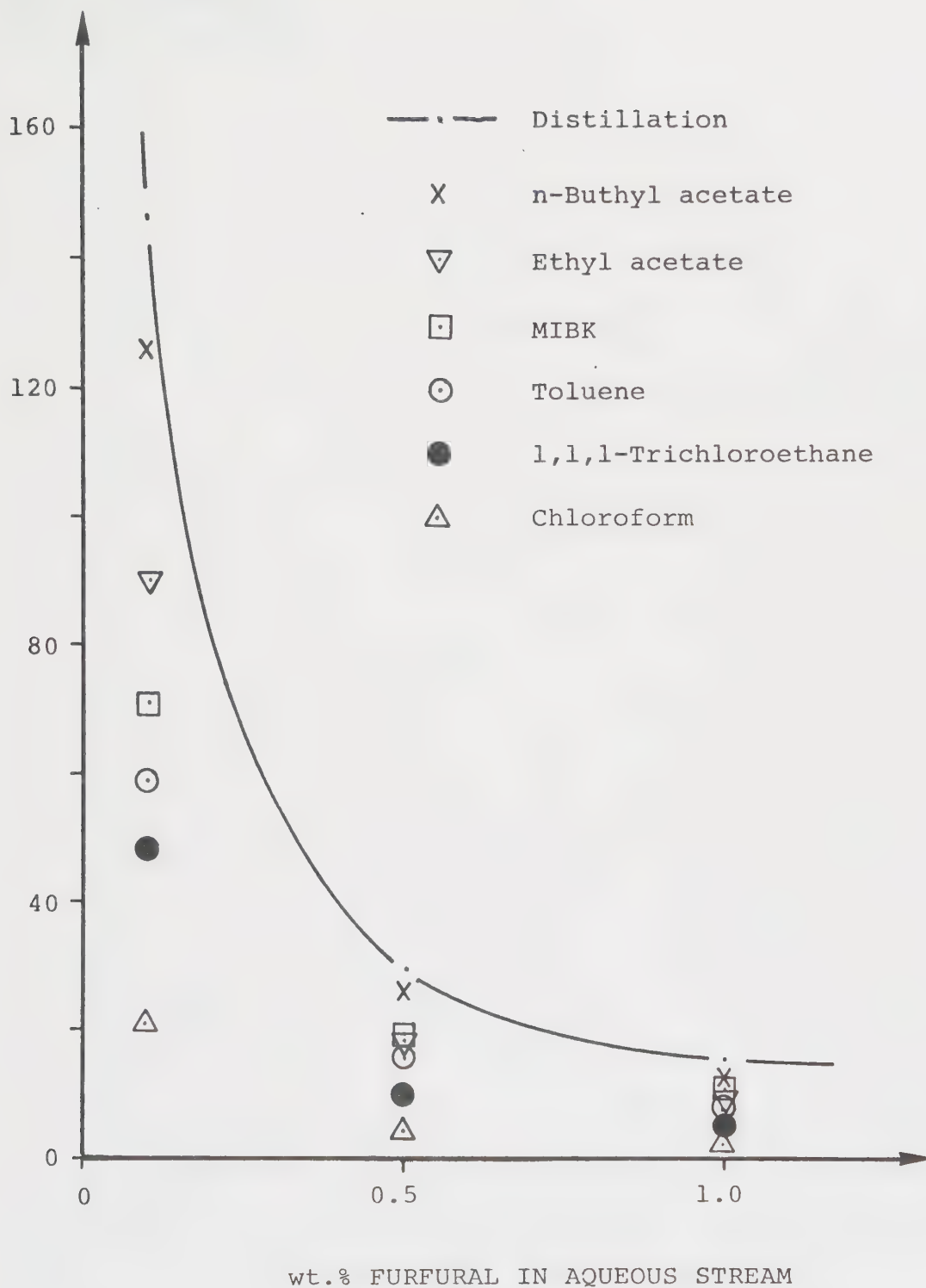


FIGURE 3: MINIMUM STEAM CONSUMPTION FOR LOW-BOILING SOLVENTS

STEAM CONSUMPTION
(ton/ton furfural)

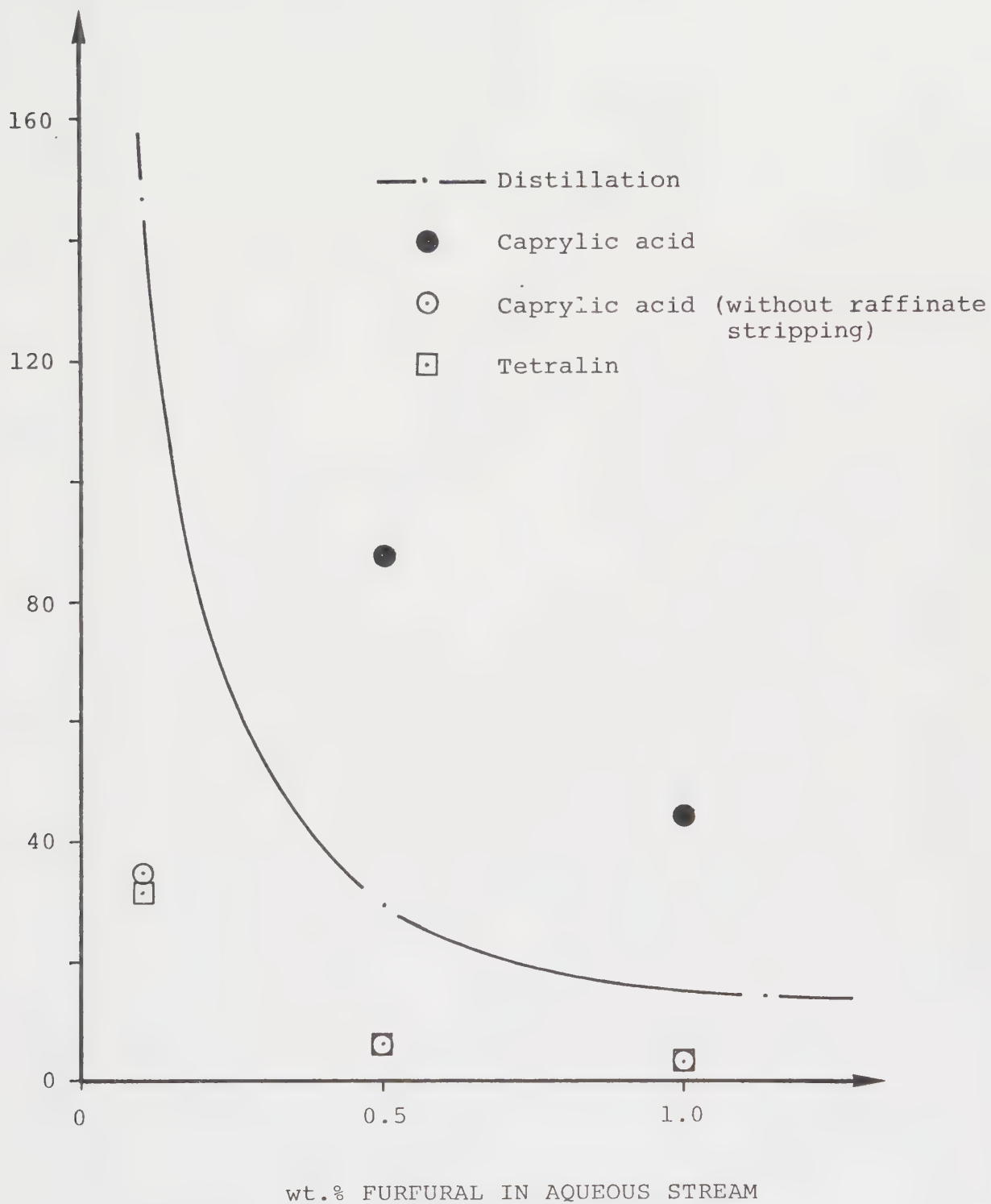


FIGURE 4: MINIMUM STEAM CONSUMPTION FOR HIGH-BOILING SOLVENTS

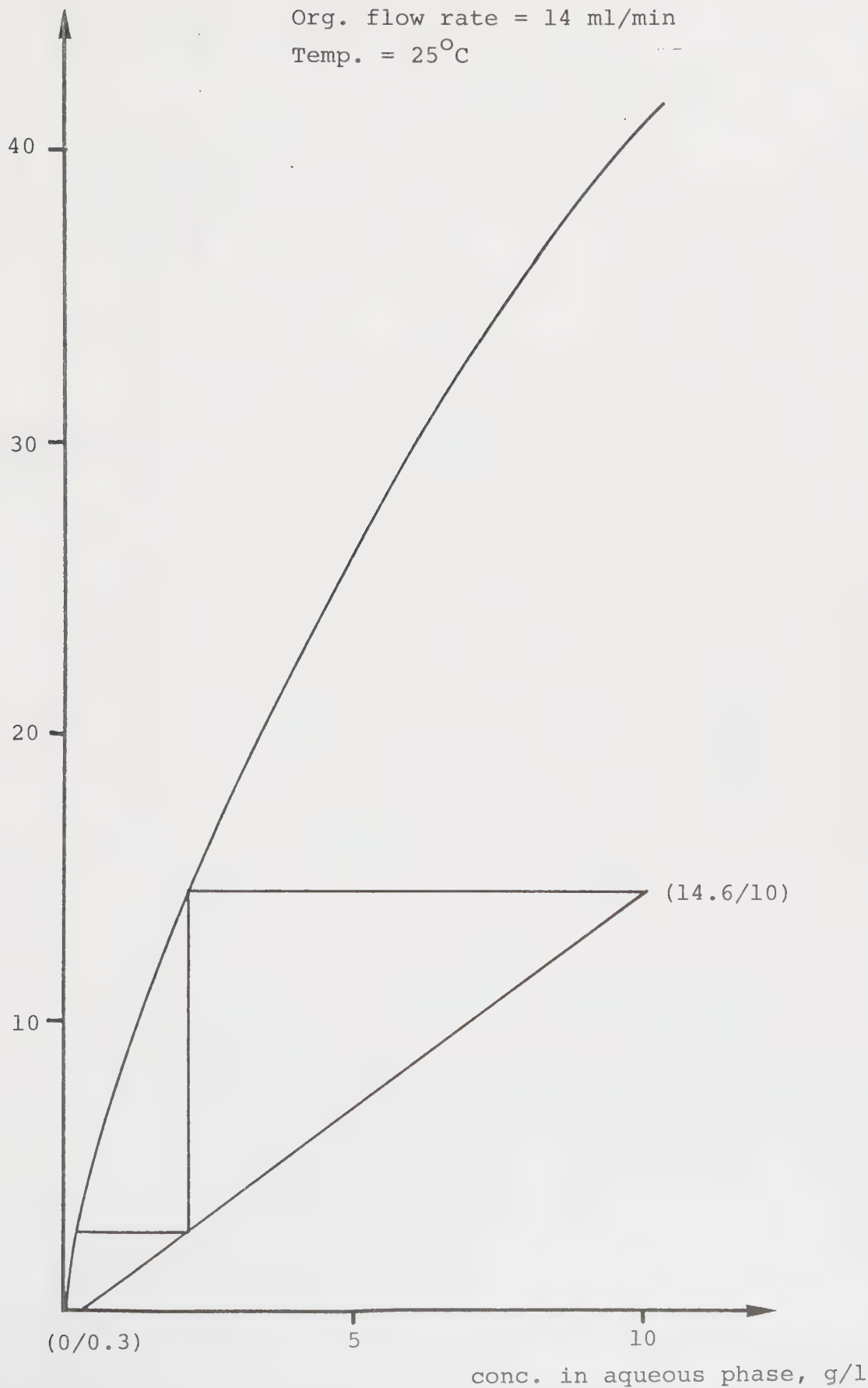
FIGURE 5: EXTRACTION OF ACETIC ACID WITH
50 VOL % ALAMINE 336 + 2-ETHYLHEXANOL
RESULT FROM EXPERIMENTAL RUN IN A
2 STAGE MIXER-SETTLER

conc. in organic phase, g/l

Aq. flow rate = 21 ml/min

Org. flow rate = 14 ml/min

Temp. = 25°C



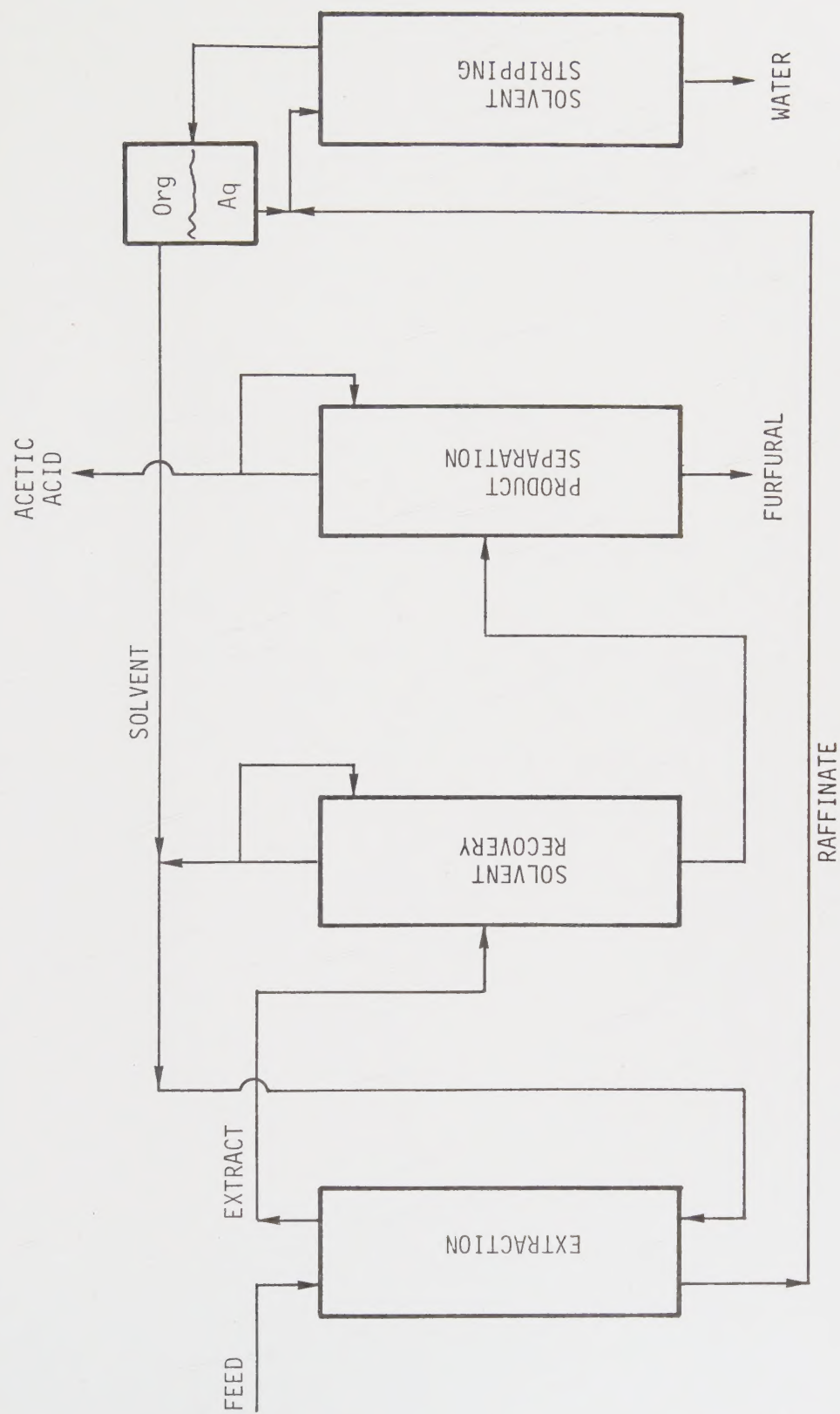


FIGURE 6: SIMULTANEOUS EXTRACTION OF ACETIC ACID AND FURFURAL WITH ETHYL ACETATE

